

# Electrochemistry

## What You'll Learn

- ▶ You will learn how oxidation–reduction reactions produce electric current.
- ▶ You will determine the voltage of the current produced by pairs of redox half-reactions.
- ▶ You will determine the direction of current flow for a particular pair of redox half-reactions.
- ▶ You will investigate how electric current can be used to carry out redox reactions.

## Why It's Important

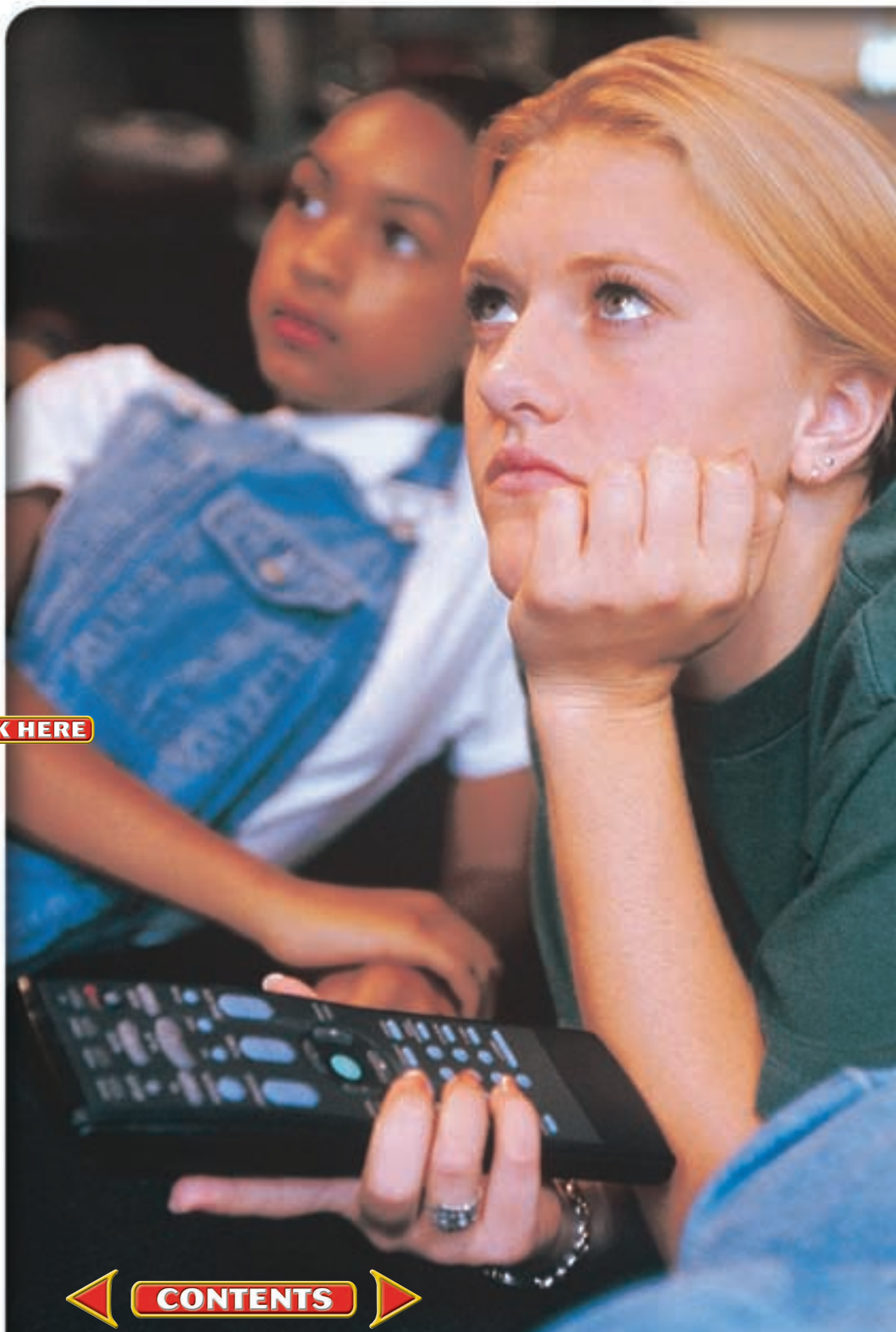
You've probably used aluminum foil to cover food, and most kids have hidden under a blanket to read by flashlight. The manufacturing process for aluminum and the light from your flashlight involve electrochemistry.

**CLICK HERE**



Visit the Chemistry Web site at [science.glencoe.com](http://science.glencoe.com) to find links about electrochemistry.

You can look around you to see how important electricity is, from the lights in the room to the batteries that power the remote control, to the manufacturing processes that produce consumer goods. Electrochemistry is one method by which electricity can be generated for use.



## DISCOVERY LAB



### Materials

lemon pieces  
zinc metal strip  
copper metal strip  
voltmeter with leads

### A Lemon Battery?

**Y**ou can purchase a handy package of portable power at any convenience store—a battery. You also can craft a working battery from a lemon. How are these power sources alike?

### Safety Precautions



Always wear an apron and safety goggles in the lab. Use caution with electricity.

### Procedure

1. Insert the zinc and copper strips into the lemon, about 2 cm apart from each other.
2. Attach the black lead from a voltmeter to the zinc and the red lead to the copper. Read and record the potential difference (voltage) from the voltmeter.
3. Remove one of the metals from the lemon and observe what happens to the potential difference on the voltmeter.

### Analysis

What is the purpose of the zinc and copper metals? What is the purpose of the lemon?

## Section

## 21.1

## Voltaic Cells

### Objectives

- **Describe** a way to obtain electrical energy from a redox reaction.
- **Identify** the parts of a voltaic cell and explain how each part operates.
- **Calculate** cell potentials and **determine** the spontaneity of redox reactions.

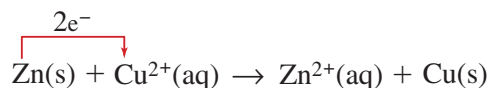
### Vocabulary

salt bridge  
electrochemical cell  
voltaic cell  
half-cell  
anode  
cathode  
reduction potential  
standard hydrogen electrode  
battery

You now know much of the basic chemistry on which advanced chemistry is based. This chapter introduces an important branch of chemistry called electrochemistry. Electrochemistry is the study of the process by which chemical energy is converted to electrical energy and vice versa.

### Redox in Electrochemistry

In Chapter 20, you learned that all redox reactions involve a transfer of electrons from the species that is oxidized to the species that is reduced. The **DISCOVERY LAB** illustrates the simple redox reaction in which zinc atoms are oxidized to form  $\text{Zn}^{2+}$  ions. The two electrons donated from each zinc atom are accepted by a  $\text{Cu}^{2+}$  ion, which changes to an atom of copper metal. The following net ionic equation illustrates the electron transfer that occurs.



Two half-reactions make up this redox process:



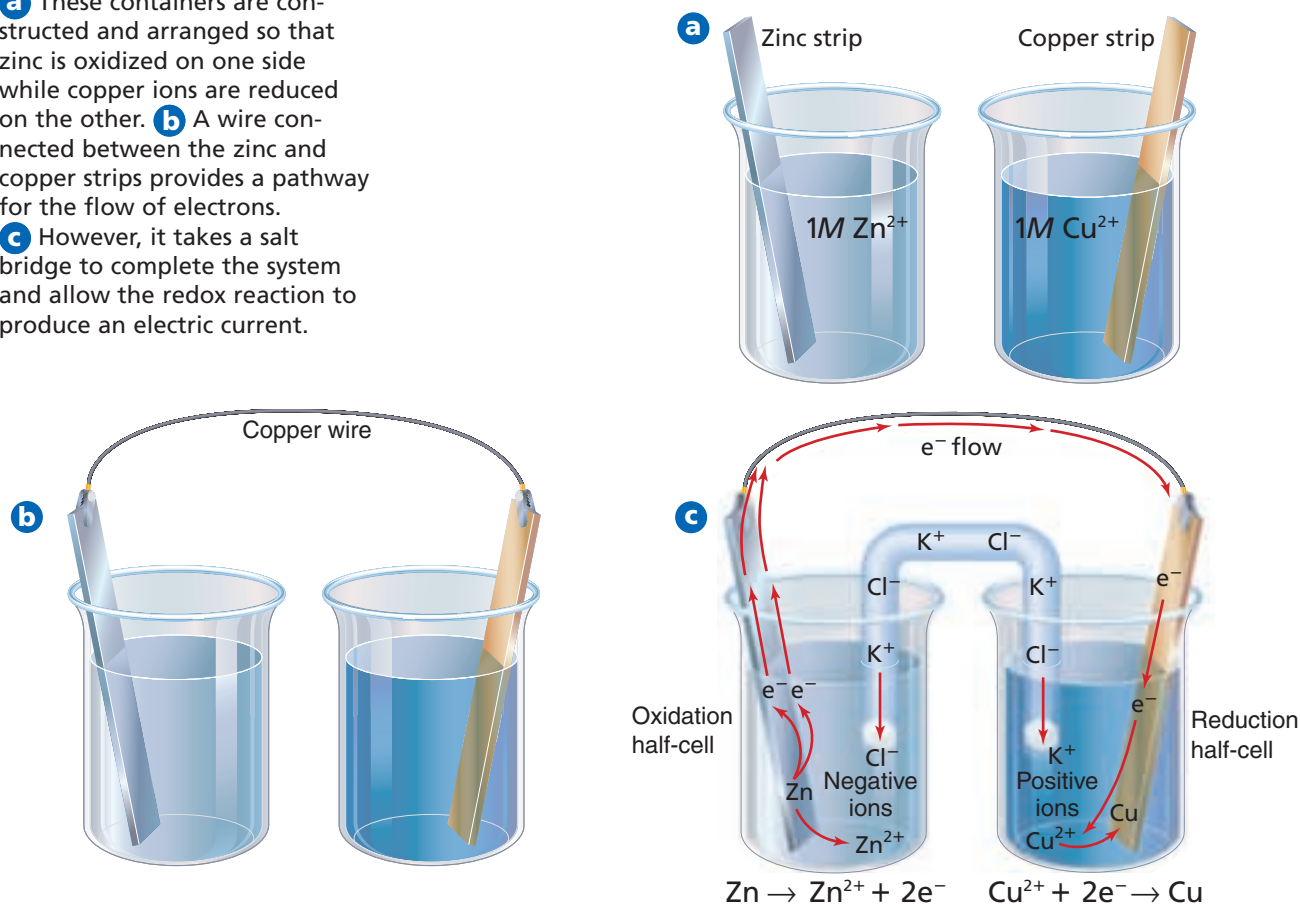
What do you think would happen if you separated the oxidation half-reaction from the reduction half-reaction? Can redox occur? Consider **Figure 21-1a** in which a zinc strip is immersed in a solution of zinc sulfate and a copper strip is immersed in a solution of copper(II) sulfate. Two problems prohibit a redox reaction in this situation. First, with this setup there is no way for zinc atoms to transfer electrons to copper(II) ions. This problem can be solved by connecting a metal wire between the zinc and copper strips, as shown in **Figure 21-1b**. The wire serves as a pathway for electrons to flow from the zinc strip to the copper strip.

Even with the conducting wire, another problem exists that prohibits the redox reaction. A positive charge builds up in one solution and a negative charge builds up in the other. The buildup of positive zinc ions on the left prohibits the oxidation of zinc atoms. On the other side, the buildup of negative ions prohibits the reduction of copper ions. To solve this problem a salt bridge must be built into the system. A **salt bridge** is a pathway constructed to allow the passage of ions from one side to another, as shown in **Figure 21-1c**. A salt bridge consists of a tube containing a conducting solution of a soluble salt, such as KCl, held in place by an agar gel or other form of plug. The ions can move through the plug but the solutions in the two beakers cannot mix.

When the metal wire and the salt bridge are in place, electrons flow through the wire from the oxidation half-reaction to the reduction half-reaction while positive and negative ions move through the salt bridge. A flow of charged particles, such as electrons, is called an electric current. Take a minute to identify the electric current in **Figure 21-1**. The flow of electrons through the wire and the flow of ions through the salt bridge make up the electric current. The energy

**Figure 21-1**

- a** These containers are constructed and arranged so that zinc is oxidized on one side while copper ions are reduced on the other. **b** A wire connected between the zinc and copper strips provides a pathway for the flow of electrons.
- c** However, it takes a salt bridge to complete the system and allow the redox reaction to produce an electric current.





of the flowing electrons can be put to use in lighting a bulb or running an electric motor.

The completed device shown in **Figure 21-1c** is an electrochemical cell. An **electrochemical cell** is an apparatus that uses a redox reaction to produce electrical energy or uses electrical energy to cause a chemical reaction. A **voltaic cell** is a type of electrochemical cell that converts chemical energy to electrical energy by a spontaneous redox reaction. **Figure 21-2** shows a version of the original voltaic cell as devised by its inventor Alessandro Volta.

## Chemistry of Voltaic Cells

An electrochemical cell consists of two parts, called **half-cells**, in which the separate oxidation and reduction reactions take place. Each half-cell contains an electrode, which is the object that conducts electrons to or from another substance, usually a solution of ions. In **Figure 21-1**, the beaker with the zinc electrode is where the oxidation part of the redox reaction takes place. The beaker with the copper electrode is where the reduction part of the reaction takes place. The reaction that takes place in each half-cell is the half-reaction, sometimes called half-cell reaction, that you studied in Chapter 20. The electrode where oxidation takes place is called the **anode** of the cell. The electrode where reduction takes place is called the **cathode** of the cell. Which beaker in **Figure 21-1** contains the anode and which contains the cathode?

Recall from Chapter 16 that an object's potential energy is due to its position or composition. In electrochemistry, electrical potential energy is a measure of the amount of current that can be generated from a voltaic cell to do work. Electric charge can flow between two points only when a difference in electrical potential energy exists between the two points. In an electrochemical cell, these two points are the two electrodes. The potential difference of a voltaic cell is an indication of the energy that is available to move electrons from the anode to the cathode.

To better understand this concept, consider the analogy illustrated in **Figure 21-3**. A golf ball that lands on a hillside will roll downhill into a low spot because a difference in gravitational potential energy exists between the two points. The kinetic energy attained by a golf ball rolling down a hill is determined by the difference in height (potential energy) between the high point and the low point. Similarly, the energy of the electrons flowing from anode to cathode in a voltaic cell is determined by the

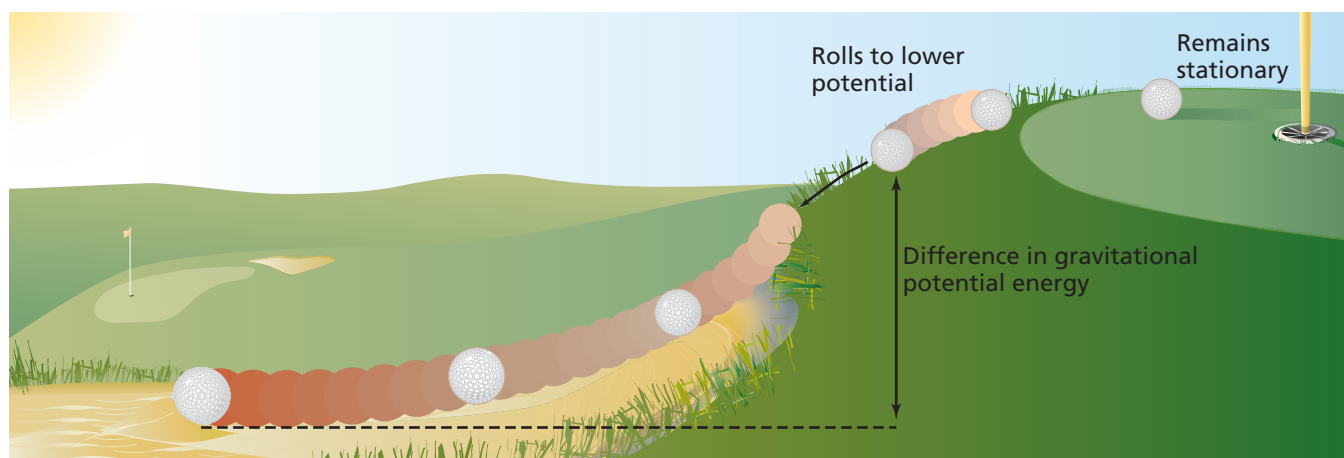


**Figure 21-2**

The voltaic cell is named for Alessandro Volta (1745–1827), the Italian physicist who is credited with its invention in 1800.

**Figure 21-3**

In this illustration of gravitational potential, we can say that the golf ball has potential energy relative to the bottom of the hill because there is a difference in the height position of the ball from the top of the hill to the bottom. Similarly, an electrochemical cell has potential energy to produce a current because there is a difference in the ability of the electrodes to move electrons from the anode to the cathode.





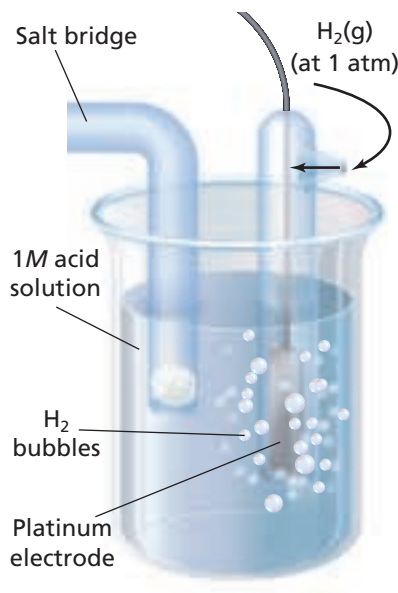
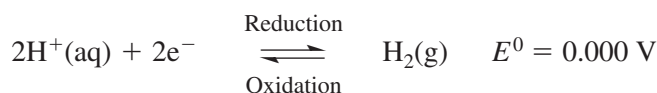
Go to the **Chemistry Interactive CD-Rom** to find additional resources for this chapter.

difference in electrical potential between the two electrodes. In redox terms, the voltage of a cell is determined by the difference in the tendency of the electrode material to accept electrons.

Thinking again of the golf ball analogy, the force of gravity causes the ball always to roll downhill to a lower energy state, not uphill to a higher energy state. In other words, the golf ball rolling process occurs spontaneously only in the downhill direction. In the zinc–copper cell under standard conditions, copper(II) ions at the cathode accept electrons more readily than the zinc ions at the anode. In other words, the redox reaction occurs spontaneously only when the electrons flow from the zinc to the copper.

## Calculating Electrochemical Cell Potential

You know from the previous chapter that the gain of electrons is called reduction. Building on this fact, we can call the tendency of a substance to gain electrons its **reduction potential**. The reduction potential of an electrode, measured in volts, cannot be determined directly because the reduction half-reaction must be coupled with an oxidation half-reaction. When these half-reactions are coupled, the voltage corresponds to the *difference* in potential between the half-reactions. The electrical potential difference between two points is expressed in volts (V). Long ago, chemists decided to measure the reduction potential of all electrodes against one standard electrode, the standard hydrogen electrode. The **standard hydrogen electrode** consists of a small sheet of platinum immersed in an HCl solution that has a hydrogen ion concentration of 1M. Hydrogen gas at a pressure of 1 atm is bubbled in and the temperature is maintained at 25°C, as shown in **Figure 21-4**. The potential (also called the standard reduction potential) of this standard hydrogen electrode is defined as 0 V. This electrode can act as an oxidation half-reaction or a reduction half-reaction, depending upon the half-cell to which it is connected. The reactions at the hydrogen electrode are



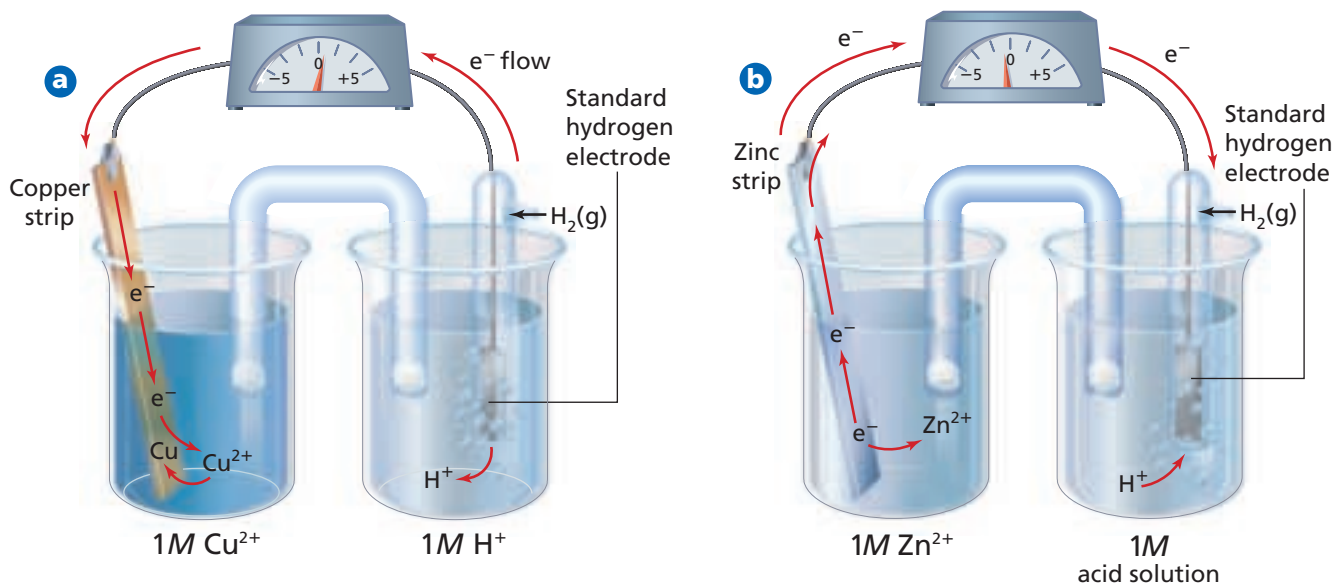
**Figure 21-4**

A standard hydrogen electrode consists of a platinum electrode with hydrogen gas at 1 atm pressure bubbling into an acidic solution that is 1M in hydrogen ions. The reduction potential for this configuration is 0 V.

Over the years, chemists have measured and recorded the standard reduction potentials, abbreviated  $E^0$ , of many different half-cells. **Table 21-1** lists some common half-cell reactions in order of increasing reduction potential. The values in the table are based on using the half-cell reaction that is being measured as the cathode and the standard hydrogen electrode as the anode. All of the half-reactions in **Table 21-1** are written as reductions. However, in any voltaic cell, which always contains two half-reactions, the half-reaction with the lower reduction potential will proceed in the opposite direction and will be an oxidation reaction. In other words, the half-reaction that is more positive will proceed as a reduction and the half-reaction that is more negative will proceed as an oxidation.

**Table 21-1**

Standard Reduction Potentials at 25°C, 1 atm, and 1M Ion Concentration			
Half-reaction	$E^0$ (V)	Half-reaction	$E^0$ (V)
$\text{Li}^+ + \text{e}^- \rightarrow \text{Li}$	-3.0401	$\text{Sn}^{4+} + 2\text{e}^- \rightarrow \text{Sn}^{2+}$	0.151
$\text{Cs}^+ + \text{e}^- \rightarrow \text{Cs}$	-3.026	$\text{Cu}^{2+} + \text{e}^- \rightarrow \text{Cu}^+$	0.153
$\text{K}^+ + \text{e}^- \rightarrow \text{K}$	-2.931	$\text{SO}_4^{2-} + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{SO}_3 + \text{H}_2\text{O}$	0.172
$\text{Ba}^{2+} + 2\text{e}^- \rightarrow \text{Ba}$	-2.912	$\text{Bi}^{3+} + 3\text{e}^- \rightarrow \text{Bi}$	0.308
$\text{Ca}^{2+} + 2\text{e}^- \rightarrow \text{Ca}$	-2.868	$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$	0.3419
$\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$	-2.71	$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$	0.401
$\text{Mg}^{2+} + 2\text{e}^- \rightarrow \text{Mg}$	-2.372	$\text{Cu}^+ + \text{e}^- \rightarrow \text{Cu}$	0.521
$\text{Ce}^{3+} + 3\text{e}^- \rightarrow \text{Ce}$	-2.336	$\text{I}_2 + 2\text{e}^- \rightarrow 2\text{I}^-$	0.5355
$\text{H}_2 + 2\text{e}^- \rightarrow 2\text{H}^-$	-2.323	$\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2$	0.695
$\text{Nd}^{3+} + 3\text{e}^- \rightarrow \text{Nd}$	-2.1	$\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$	0.771
$\text{Be}^{2+} + 2\text{e}^- \rightarrow \text{Be}$	-1.847	$\text{NO}_3^- + 2\text{H}^+ + \text{e}^- \rightarrow \text{NO}_2 + \text{H}_2\text{O}$	0.775
$\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$	-1.662	$\text{Hg}_2^{2+} + 2\text{e}^- \rightarrow 2\text{Hg}$	0.7973
$\text{Mn}^{2+} + 2\text{e}^- \rightarrow \text{Mn}$	-1.185	$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$	0.7996
$\text{Cr}^{2+} + 2\text{e}^- \rightarrow \text{Cr}$	-0.913	$\text{Hg}^{2+} + 2\text{e}^- \rightarrow \text{Hg}$	0.851
$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$	-0.8277	$2\text{Hg}_2^{2+} + 2\text{e}^- \rightarrow \text{Hg}_2^{2+}$	0.920
$\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$	-0.7618	$\text{Pd}^{2+} + 2\text{e}^- \rightarrow \text{Pd}$	0.951
$\text{Cr}^{3+} + 3\text{e}^- \rightarrow \text{Cr}$	-0.744	$\text{NO}_3^- + 4\text{H}^+ + 3\text{e}^- \rightarrow \text{NO} + 2\text{H}_2\text{O}$	0.957
$\text{Ga}^{3+} + 3\text{e}^- \rightarrow \text{Ga}$	-0.549	$\text{Br}_2(\text{l}) + 2\text{e}^- \rightarrow 2\text{Br}^-$	1.066
$2\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{C}_2\text{O}_4$	-0.49	$\text{Ir}^{3+} + 3\text{e}^- \rightarrow \text{Ir}$	1.156
$\text{S} + 2\text{e}^- \rightarrow \text{S}^{2-}$	-0.47627	$\text{Pt}^{2+} + 2\text{e}^- \rightarrow \text{Pt}$	1.18
$\text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe}$	-0.447	$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$	1.229
$\text{Cr}^{3+} + \text{e}^- \rightarrow \text{Cr}^{2+}$	-0.407	$\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-$	1.35827
$\text{Cd}^{2+} + 2\text{e}^- \rightarrow \text{Cd}$	-0.4030	$\text{Au}^{3+} + 2\text{e}^- \rightarrow \text{Au}^+$	1.401
$\text{PbI}_2 + 2\text{e}^- \rightarrow \text{Pb} + 2\text{I}^-$	-0.365	$\text{Au}^{3+} + 3\text{e}^- \rightarrow \text{Au}$	1.498
$\text{PbSO}_4 + 2\text{e}^- \rightarrow \text{Pb} + \text{SO}_4^{2-}$	-0.3588	$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$	1.507
$\text{Co}^{2+} + 2\text{e}^- \rightarrow \text{Co}$	-0.28	$\text{Au}^+ + \text{e}^- \rightarrow \text{Au}$	1.692
$\text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni}$	-0.257	$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}$	1.776
$\text{Sn}^{2+} + 2\text{e}^- \rightarrow \text{Sn}$	-0.1375	$\text{Co}^{3+} + \text{e}^- \rightarrow \text{Co}^{2+}$	1.92
$\text{Pb}^{2+} + 2\text{e}^- \rightarrow \text{Pb}$	-0.1262	$\text{S}_2\text{O}_8^{2-} + 2\text{e}^- \rightarrow 2\text{SO}_4^{2-}$	2.010
$\text{Fe}^{3+} + 3\text{e}^- \rightarrow \text{Fe}$	-0.037	$\text{O}_3 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{O}_2 + \text{H}_2\text{O}$	2.076
$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	0.0000	$\text{F}_2 + 2\text{e}^- \rightarrow 2\text{F}^-$	2.866



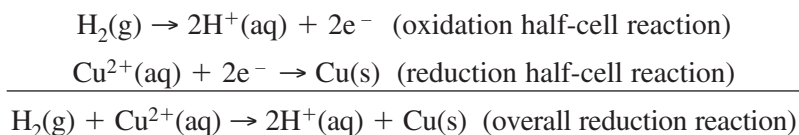
**Figure 21-5**

**a** When a  $\text{Cu}|\text{Cu}^{2+}$  electrode is connected to the hydrogen electrode, electrons flow toward the copper strip and reduce  $\text{Cu}^{2+}$  ions to Cu atoms. The voltage of this reaction is +0.342 V.

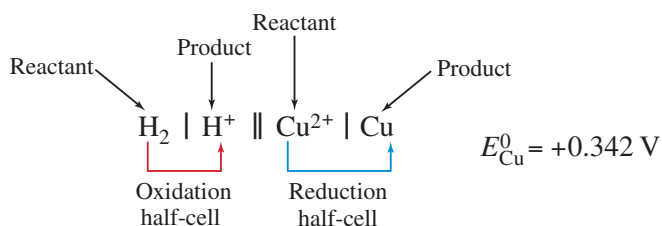
**b** When a  $\text{Zn}|\text{Zn}^{2+}$  electrode is connected to the hydrogen electrode, electrons flow away from the zinc strip and zinc atoms are oxidized to  $\text{Zn}^{2+}$  ions. The voltage of this reaction is -0.762 V.

The electrode being measured also must be under standard conditions; that is, immersed in a 1M solution of its ions at 25°C and 1 atm pressure. The superscript zero in the notation  $E^0$  is a shorthand way of indicating “measured under standard conditions.”

With **Table 21-1**, it is possible to calculate the electrical potential of a voltaic cell having a copper electrode and a zinc electrode under standard conditions. The first step is to determine the standard reduction potential for the copper half-cell ( $E_{\text{Cu}}^0$ ). When the copper electrode is attached to a standard hydrogen electrode, as in **Figure 21-5a**, electrons flow *from* the hydrogen electrode *to* the copper electrode, and copper ions are reduced to copper metal. The  $E^0$ , measured by a voltmeter, is +0.342 V. The positive voltage indicates that  $\text{Cu}^{2+}$  ions at the copper electrode being measured accept electrons more readily than do  $\text{H}^+$  ions at the standard hydrogen electrode. From this information, you can determine where oxidation and reduction take place. In this case, oxidation takes place at the hydrogen electrode, and reduction takes place at the copper electrode. The oxidation and reduction half-cell reactions and the overall reaction are



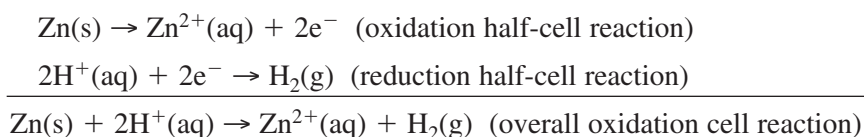
This reaction can be written in a form called cell notation to clearly describe the copper reduction reaction.



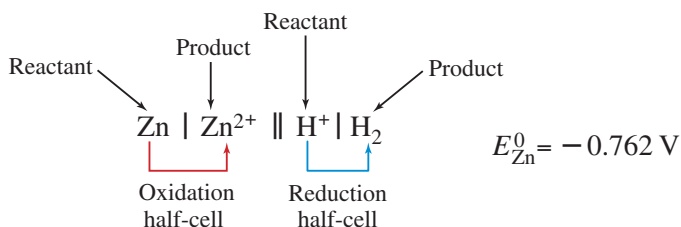
Note that the two participants in the oxidation reaction are written first and in the order they appear in the oxidation half-reaction—*reactant* | *product*.

They are followed by a double vertical line (||) indicating the wire and salt bridge connecting the half-cells. Then, the two participants in the reduction reaction are written in the same *reactant* | *product* order. Note in this example that it is customary to place a plus sign before a positive voltage to avoid confusion.

The next step is to determine the standard reduction potential for the zinc half-cell ( $E_{\text{Zn}}^0$ ). When the zinc electrode is measured against the standard hydrogen electrode under standard conditions, as in **Figure 21-5b**, electrons flow from the zinc electrode to the hydrogen electrode. The  $E^0$  of the zinc half-cell, measured by a voltmeter, is  $-0.762\text{ V}$ . This means that the  $\text{H}^+$  ions at the hydrogen electrode accept electrons more readily than do the zinc ions, and thus the hydrogen ions have a *higher* reduction potential than the zinc ions. If you remember that the hydrogen electrode is assigned a zero potential, you will realize that the reduction potential of the zinc electrode must have a negative value. Electrodes at which oxidation is carried out when connected to a hydrogen electrode have negative standard reduction potentials. How would you write the oxidation and reduction reactions and the overall zinc oxidation reaction? The reactions are written as follows.



This reaction can be written in cell notation to clearly describe the zinc oxidation reaction.



The final step is to combine the Cu and Zn half-cells as a voltaic cell, which means calculating the voltaic cell's standard potential using the following formula

$$E_{\text{cell}}^0 = E_{\text{reduction}}^0 - E_{\text{oxidation}}^0$$

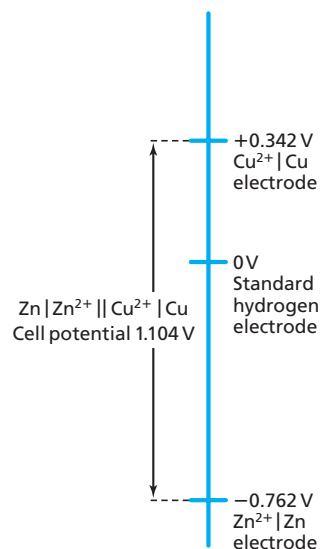
Because reduction occurred at the copper electrode and oxidation occurred at the zinc electrode, the  $E^0$  values are substituted as follows.

$$\begin{aligned} E_{\text{cell}}^0 &= E_{\text{Cu}^{2+} \mid \text{Cu}}^0 - E_{\text{Zn}^{2+} \mid \text{Zn}}^0 \\ &= 0.342\text{ V} - (-0.762\text{ V}) \\ &= +1.104\text{ V} \end{aligned}$$

**Figure 21-6** describes this potential calculation. The graph shows the zinc half-cell with the lower reduction potential (the oxidation half-reaction) and the copper half-cell with the higher reduction potential (the reduction half-reaction). You can see that the space between the two ( $E_{\text{cell}}^0$ ) is the difference between the potentials of the individual half-cells. The Example Problem that follows gives a step-by-step description of calculating cell potentials.

**Figure 21-6**

This simple graph illustrates how the overall cell potential is derived from the difference in reduction potential of two electrodes.





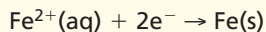
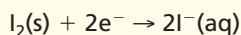
## EXAMPLE PROBLEM 21-1



Cloud seeding using iodine compounds to promote precipitation may be one way to ease severe drought conditions.

### Calculating Cell Potential

The two reduction half-reactions in this example represent the half-cells of a voltaic cell.



Determine the overall cell reaction and the standard cell potential. Write the cell chemistry using cell notation with vertical lines separating components.

#### 1. Analyze the Problem

You are given the half-cell descriptions for a voltaic cell and standard reduction potentials in **Table 21-1**. In any voltaic cell, the half-reaction with the lower reduction potential will proceed as an oxidation. With this information, you can write the overall cell reaction and calculate the standard cell potential.

##### Known

Standard reduction potentials for the half-cells

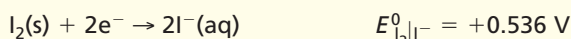
$$E_{\text{cell}}^0 = E_{\text{reduction}}^0 - E_{\text{oxidation}}^0$$

##### Unknown

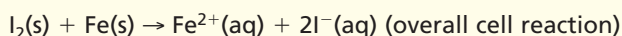
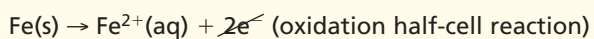
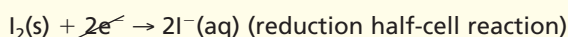
$$E_{\text{cell}}^0 = ?$$

#### 2. Solve for the Unknown

Find the standard reduction potentials of each half-reaction in a reference source such as **Table 21-1**.



Note that reduction of iodine has the higher reduction potential. This half-reaction will proceed in the forward direction as a reduction. The iron half-reaction will proceed in the reverse direction as an oxidation. Rewrite the half-reactions in the correct direction.



Balance the reaction if necessary. Note that this reaction is balanced as written.

Calculate cell standard potential.

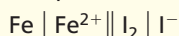
$$E_{\text{cell}}^0 = E_{\text{reduction}}^0 - E_{\text{oxidation}}^0$$

$$E_{\text{cell}}^0 = E_{\text{I}_2|\text{I}^-}^0 - E_{\text{Fe}^{2+}|\text{Fe}}^0$$

$$E_{\text{cell}}^0 = +0.536 \text{ V} - (-0.447 \text{ V})$$

$$E_{\text{cell}}^0 = +0.983 \text{ V}$$

Write the reaction using cell notation. When representing a reaction in cell notation, the species in the oxidation half-reaction are written first in the following order: reactant | product, or in this case,  $\text{Fe} | \text{Fe}^{2+}$ . The species in the reduction half-reaction are written next in the order reactant | product, or in this case,  $\text{I}_2 | \text{I}^-$ . Therefore, the complete cell is represented as

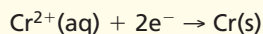
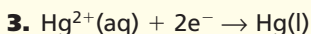
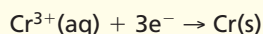
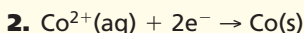
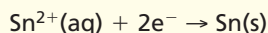
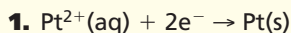


### 3. Evaluate the Answer

The standard potential for this voltaic cell seems reasonable given the reduction potentials of the half-cells that comprise it. The mathematical operations with negative numbers are correct and the answer is correct to the thousandths place.

## PRACTICE PROBLEMS

For each of these pairs of half-reactions, write the balanced equation for the overall cell reaction and calculate the standard cell potential. Express the reaction using cell notation. You may wish to refer to Chapter 20 to review writing and balancing redox equations.



For more practice calculating cell potential, go to **Supplemental Practice Problems** in Appendix A.

The **CHEMLAB** at the end of this chapter offers an opportunity to create voltaic cells and calculate cell potentials.

## Using Standard Reduction Potentials

You just practiced using the data from **Table 21-1** to calculate the standard potential (voltage) of voltaic cells by determining the difference in reduction potential of the half-cell reactions. Another important use of standard reduction potentials is to determine if a proposed reaction under standard conditions will be spontaneous. How can standard reduction potentials indicate spontaneity? Electrons in a voltaic cell always flow from the half-cell with the lower standard reduction potential to the half-cell with higher reduction potential, giving a positive cell voltage. To predict whether any proposed redox reaction will occur spontaneously, simply write the process in the form of half-reactions and look up the reduction potential of each. Use the values to calculate the potential of a voltaic cell operating with these two half-cell reactions. If the calculated potential is positive, the reaction is spontaneous. If the value is negative, the reaction is not spontaneous. However, the reverse reaction will occur because it will give a positive cell voltage and, therefore, the reverse reaction is spontaneous.

For example, use the standard reduction potentials in **Table 21-1** to calculate the potential of the cell  $\text{Li} | \text{Li}^{+} || \text{Ag}^{+} | \text{Ag}$ .

$$\begin{aligned} E_{\text{cell}}^0 &= E_{\text{Ag}^{+} | \text{Ag}}^0 - E_{\text{Li}^{+} | \text{Li}}^0 \\ &= 0.7996 \text{ V} - (-3.0401 \text{ V}) \\ &= 3.8397 \text{ V} \end{aligned}$$

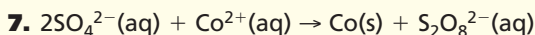
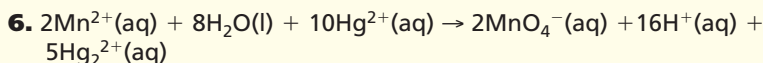
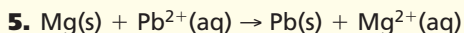
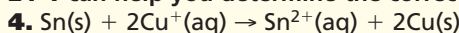
The calculated potential for the cell  $\text{Li} | \text{Li}^{+} || \text{Ag}^{+} | \text{Ag}$  is a positive number. Thus, the redox reaction in this cell will proceed spontaneously if the system is at 25°C, 1 atm, and 1M concentration.



For more practice determining if redox reactions are spontaneous, go to **Supplemental Practice Problems** in Appendix A.

## PRACTICE PROBLEMS

Calculate the cell potential to determine if each of the following balanced redox reactions is spontaneous as written. Examining the reactions in **Table 21-1** can help you determine the correct half-reactions.



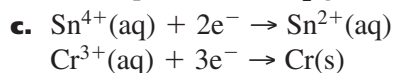
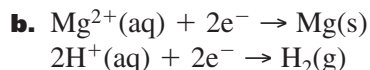
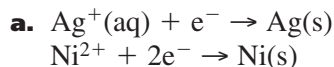
Now that you know the chemistry of voltaic cells, you may begin to see their value as a power source. It turns out that Alessandro Volta also realized the value of this chemistry. From his experimentation, Volta deduced that if one cell generates a current, several cells connected together should produce a larger current. Volta connected a series of cells by making a pile of alternating zinc plates serving as anodes and silver plates serving as cathodes separated by layers of cloth soaked with salt solution. The cloth had the same function as the salt bridge. This arrangement became known as a “voltaic pile” and was literally a “pile”, as you saw in **Figure 21-2**. Volta’s pile was the first battery. A **battery** consists of one or more electrochemical cells in a single package that generates electrical current. You’ll learn more about batteries in the next section of this chapter.

## Section 21.1 Assessment

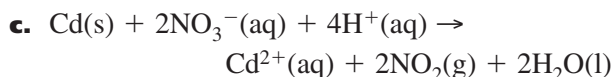
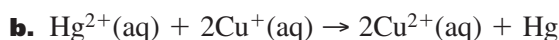
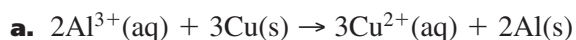
8. Under what conditions can a redox reaction be used to cause an electric current to flow through a wire?

9. What are the components of a voltaic cell? What is the role of each component in the operation of the cell?

10. Write the balanced equation for the spontaneous cell reaction that will occur in a cell with these reduction half-reactions.



11. These equations represent overall cell reactions. Determine the standard potential for each cell and identify the reactions as spontaneous or nonspontaneous as written.



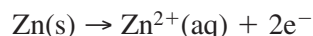
12. **Thinking Critically** The reduction half-reaction  $\text{I}_2 + 2\text{e}^- \rightarrow 2\text{I}^-$  has a lower standard reduction potential than the reduction half-reaction  $\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-$ . In terms of electron transfer, what is the significance of this difference in reduction potentials? Which of these reactions would produce the higher voltage in a cell in which the oxidation half-reaction is  $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$ ? Explain your choice.

13. **Predicting** Suppose you have a half-cell of unknown composition, but you know the cell is at standard conditions. You connect it to a copper–copper(II) sulfate half-cell, also at standard conditions, and the voltmeter in the circuit reads 0.869 V. Is it possible to predict the probable composition of the unknown half-cell? Explain your answer.

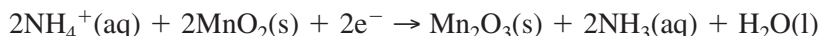
How many different uses of batteries can you identify? Batteries power flashlights, remote controls, calculators, hearing aids, portable CD players, heart pacemakers, smoke and carbon monoxide detectors, and video cameras, to name a few. Batteries in cars and trucks provide electric energy to start the engine and power the vehicle's many electric lights, sound system, and other accessories, even when the engine is not running.

## Dry Cells

In Section 21.1, you learned that the simplest form of a battery is a single voltaic cell. The word *battery* once referred only to a group of single cells in one package, such as the 9 V battery. Today, however, the word *battery* refers to both single cells and packages of several cells, such as the batteries shown in **Figure 21-7**. From the time of its invention in the 1860s until recently, the most commonly used voltaic cell was the zinc–carbon dry cell, shown in **Figure 21-8** on the next page. A **dry cell** is an electrochemical cell in which the electrolyte is a moist paste. The paste in a zinc–carbon dry cell consists of zinc chloride, manganese(IV) oxide, ammonium chloride, and a small amount of water inside a zinc case. The zinc shell is the cell's anode, where the oxidation of zinc metal occurs. The following equation describes the oxidation half-cell reaction for this dry cell.



A carbon (graphite) rod in the center of the dry cell serves as the cathode, but the reduction half-cell reaction takes place in the paste. An electrode made of a material that does not participate in the redox reaction is called an inactive electrode. The carbon rod in this type of dry cell is an inactive cathode. (Contrast this with the zinc case, which is an active anode because the zinc is oxidized.) The reduction half-cell reaction for this dry cell follows.



Chemists know that the reduction reaction is more complex than this equation shows, but they still do not know precisely what happens in the reaction. A spacer, made of a porous material and damp from the liquid in the paste, separates the paste from the zinc anode. The spacer acts as a salt bridge to

## Objectives

- **Describe** the structure, composition, and operation of the typical carbon–zinc dry cell battery.
- **Distinguish** between primary and secondary batteries and give two examples of each type.
- **Explain** the structure and operation of the hydrogen–oxygen fuel cell.
- **Describe** the process of corrosion of iron and methods to prevent corrosion.

## Vocabulary

dry cell  
primary battery  
secondary battery  
fuel cell  
corrosion  
galvanizing



**Figure 21-7**

The small batteries (AA, AAA, C, and D) that power household appliances and small electrical devices consist of single electrochemical cells. The large battery of a car, however, consists of six electrochemical cells connected together.





**Figure 21-8**

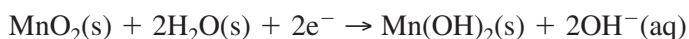
The so-called dry cell actually contains a moist paste in which the cathode half-reaction takes place. **a** In the zinc-carbon dry cell, the zinc case acts as the anode. **b** The alkaline battery uses powdered zinc and is contained in a steel case. **c** Although it looks different, the mercury battery is much like the alkaline battery, except that the mercury battery uses mercury(II) oxide (HgO) in the cathode instead of manganese(IV) oxide (MnO<sub>2</sub>).

allow the transfer of ions, much like the model voltaic cell you studied in Section 21.1. The zinc-carbon dry cell produces a voltage of 1.5 V, until the reduction product ammonia comes out of its aqueous solution as a gas. At that point, the voltage drops to a level that makes the battery useless.

As new research and development bring about newer and more efficient products, the standard zinc-carbon dry cell has begun to give way to the alkaline dry cell, also shown in **Figure 21-8b**. The alkaline cell oxidizes zinc, but the zinc is in a powdered form. Why might the powdered zinc be an advantage? The powdered form, as you learned in Chapter 17, provides more surface area for reaction. The zinc is mixed in a paste with potassium hydroxide, a strong alkali base, and the paste is contained in a steel case. The cathode mixture is manganese(IV) oxide, also mixed with potassium hydroxide. The zinc anode half-cell reaction is

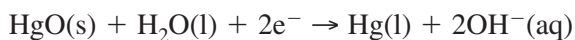


The cathode half-cell reaction is



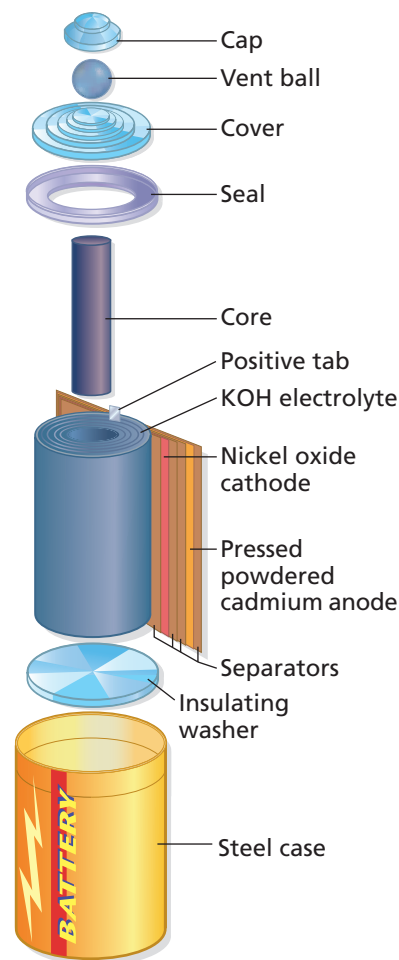
Alkaline batteries do not need the carbon rod cathode and are, therefore, smaller and more compatible with smaller devices.

The mercury battery shown in **Figure 21-8c** is smaller yet and is used to power devices such as hearing aids and calculators. The mercury battery uses the same anode half-reaction as the alkaline battery, with this cathode half-reaction.

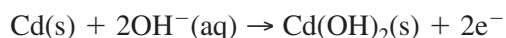


## Primary and secondary batteries

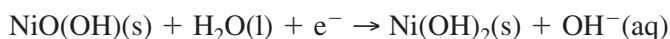
Batteries are divided into two types depending on their chemical processes. The zinc–carbon, alkaline–zinc, and mercury cells are classified as primary batteries. **Primary batteries** produce electric energy by means of redox reactions that are not easily reversed. These cells deliver current until the reactants are gone, and then the battery is discarded. Batteries that are rechargeable depend on reversible redox reactions. They are called **secondary batteries**. What devices can you identify that use secondary batteries? A car battery and the battery in a laptop computer are examples of secondary batteries, sometimes called *storage batteries*.



The storage batteries that power devices such as cordless drills and screwdrivers, shavers, and camcorders are usually nickel–cadmium rechargeable batteries, sometimes called NiCad batteries, as shown in **Figure 21-9**. For maximum efficiency, the anode and cathode are long, thin ribbons of material separated by a layer that ions can pass through. The ribbons are wound into a tight coil and packaged into a steel case. The anode reaction that occurs when the battery is used to generate electric current is the oxidation of cadmium in the presence of a base.



The cathode reaction is the reduction of nickel from the +3 to the +2 oxidation state.

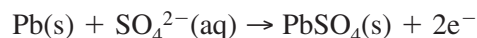


When the battery is recharged, these reactions are reversed.

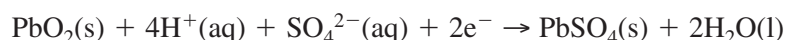
## Lead–Acid Storage Battery

Another common storage battery is the lead–acid battery. The standard automobile battery is an example of a lead–acid battery. Most auto batteries of this type contain six cells that generate about 2 V each for a total output of 12 V. The anode of each cell consists of two or more grids of porous lead, and the cathode consists of lead grids filled with lead(IV) oxide. This type of battery probably should be called a lead–lead(IV) oxide battery, but the term *lead–acid* is commonly used because the battery’s electrolyte is a solution of sulfuric acid.

The following equation represents the oxidation half-cell reaction at the anode where lead is oxidized from the zero oxidation state to the +2 oxidation state.

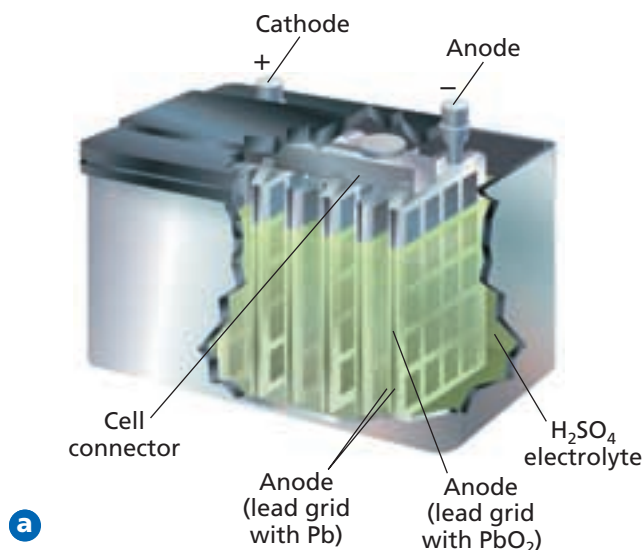


The reduction of lead from the +4 to the +2 oxidation state takes place at the cathode. The half-cell reaction for the cathode is



**Figure 21-9**

Cordless tools and phones often use rechargeable batteries, such as the NiCad type, for power. The battery pack in the phone is recharged when the handset is replaced on the base. In this case, the base is plugged into an electrical outlet, which supplies the power to drive the nonspontaneous recharge reaction.



**Figure 21-10**

**a** Lead–acid batteries contain lead plates and lead(IV) oxide plates. The electrolyte is a solution of sulfuric acid. When the battery is in use, the sulfuric acid is depleted and the electrolyte becomes less dense. **b** The condition of the battery can be checked by measuring the density of the electrolyte solution.

The overall reaction is



By looking at the half-cell reactions, you can see that lead(II) sulfate ( $\text{PbSO}_4$ ) is the reaction product in both oxidation and reduction. Also,  $\text{Pb}$ ,  $\text{PbO}_2$ , and  $\text{PbSO}_4$  are solid substances, so they stay in place where they are formed. Thus, whether the battery is discharging or charging, the reactants are available where they are needed. Sulfuric acid serves as the electrolyte in the battery, but, as the overall cell equation shows, it is depleted as the battery generates electric current. For this reason, it is possible to measure a battery's state of charge by measuring the density of the electrolyte. Sulfuric acid ( $\text{H}_2\text{SO}_4$ ) has almost twice the density of water. As the  $\text{H}_2\text{SO}_4$  is used up, the solution becomes less dense. What happens when the battery is recharging? In this case, the reactions reverse, forming lead and lead(IV) oxide and releasing sulfuric acid, shown as  $4\text{H}^+ + 2\text{SO}_4^{2-}$  in the equation.

The lead-storage battery shown in **Figure 21-10** is a good choice for motor vehicles because it provides a large initial supply of energy to start the engine, has a long shelf-life, and is reliable at low temperatures.

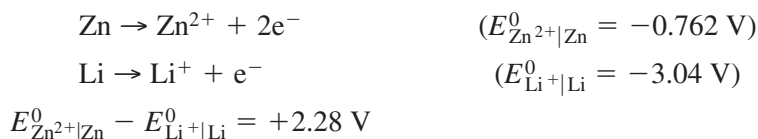
## Lithium Batteries

Although lead–acid batteries are reliable and suitable for many applications, the recent trend has been, and continues to be, the development of batteries with less mass and higher capacity to power devices from wristwatches to electric cars. For applications where a battery is the key component and must provide a significant amount of power, such as for the operation of electric cars, lead–acid batteries are too heavy to be feasible.

The solution is to develop lightweight batteries that store a large amount of energy for their size. Scientists and engineers have focused a lot of attention on the element lithium for two main reasons: lithium is the lightest



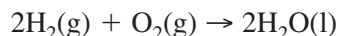
known metal and lithium has the lowest standard reduction potential of the metallic elements,  $-3.04\text{ V}$  (see **Table 21-1**). This means that a battery that oxidizes lithium at the anode can generate almost 2.3 volts more than a similar battery in which zinc is oxidized. Compare the two oxidation half-reactions and their standard reduction potentials.



Lithium batteries can be either primary or secondary, depending on which reduction reactions are coupled to the oxidation of lithium. For example, some lithium batteries use the same cathode reaction as zinc–carbon dry cells, the reduction of manganese(IV) oxide ( $\text{MnO}_2$ ) to manganese(III) oxide ( $\text{Mn}_2\text{O}_3$ ). These batteries produce electric current at about 3 V compared to 1.5 V for zinc–carbon cells. Lithium batteries last much longer than other kinds of batteries. As a result, they are often used in watches, computers, and cameras to maintain time, date, memory, and personal settings—even when the device is turned off.

## Fuel Cells

The dynamic reaction in which a fuel, such as hydrogen gas or methane, burns may seem quite different from the relatively calm redox reactions that take place in batteries. However, the burning of fuel shown in **Figure 21-11** also is an oxidation–reduction reaction. What happens when hydrogen burns in air?



In this reaction, hydrogen is oxidized from zero oxidation state in  $\text{H}_2$  to a +1 oxidation state in water. Oxygen is reduced from zero oxidation state in  $\text{O}_2$  to  $-2$  in water. When hydrogen burns in air, hydrogen atoms form polar covalent bonds with oxygen, in effect sharing electrons directly with the highly electronegative oxygen atom. This reaction is analogous to the reaction that occurs when a zinc strip is immersed in a solution of copper(II) sulfate. Electrons from the oxidation of zinc transfer directly to copper(II) ions, reducing them to atoms of copper metal. Because the zinc atoms and copper ions are in close contact, there is no reason for electrons to flow through an external circuit.

You saw in Section 21.1 how the oxidation and reduction processes can be separated to cause electrons to flow through a wire. The same can be done so that a fuel “burns” in a highly controlled way while generating electric current. A **fuel cell** is a voltaic cell in which the oxidation of a fuel is used to produce electric energy. Although many people believe the fuel cell to be a modern invention, the first one was demonstrated in 1839 by William Grove (1811–1896), a British electrochemist. He called his cell a “gas battery.” It was not until the 1950s, when scientists began working earnestly on the space program, that efficient, practical fuel cells were developed. As in other voltaic



## Careers Using Chemistry

### Electrochemist

*Do you like to experiment with batteries and other devices that generate electric current? Then consider becoming an electrochemist.*

Electrochemists study electrons. The presence, absence, and movement of electrons often determine whether a chemical reaction will take place. Electrochemists work with semiconductors, medical sensors, metal plating, and anti-corrosion technology in the automobile, medical, and computer industries and in other fields.

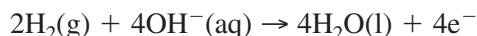
**Figure 21-11**

This oxyhydrogen torch uses hydrogen as its fuel and oxidizes hydrogen to water in a vigorous combustion reaction. Like the torch, fuel cells also oxidize hydrogen to water, but fuel cells operate at a much more controlled rate.



cells, an electrolyte is required so that ions can migrate between electrodes. In the case of the fuel cell, a common electrolyte is an alkaline solution of potassium hydroxide.

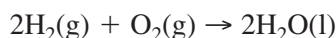
In a fuel cell, each electrode is a hollow chamber of porous carbon walls that allow contact between the inner chamber and the electrolyte surrounding it. The walls of the chamber also contain catalysts, such as powdered platinum or palladium, which speed up the reactions. These catalysts are similar to those in an automobile's catalytic converter, which you read about in Chapter 17. The following oxidation half-reaction takes place at the anode.



The reaction uses the hydroxide ions abundant in the alkaline electrolyte and releases electrons to the anode. Electrons from the oxidation of hydrogen flow through the external circuit to the cathode where the following reduction half-reaction takes place



The electrons allow the reduction of oxygen in the presence of water to form four hydroxide ions, which replenish the hydroxide ions used up at the anode. By combining the two half-reactions, the overall cell reaction is determined. As you can see, it is the same as the equation for the burning of hydrogen in oxygen.



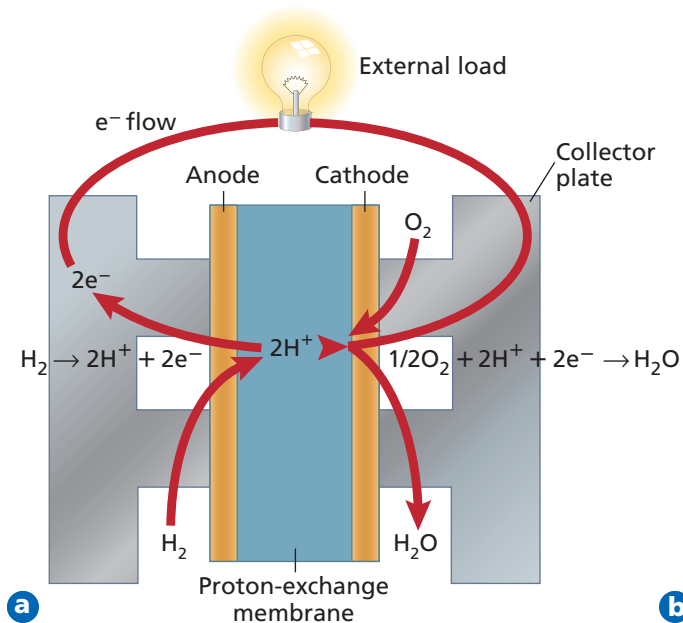
The hydrogen–oxygen fuel cell also burns hydrogen in a sense, but the burning is controlled so that most of the chemical energy is converted to electrical energy, not to heat.

In understanding fuel cells, it might be helpful to think of them as reaction chambers into which oxygen and hydrogen are fed from outside sources and from which the reaction product, water, is removed. Because the fuel for the cell is provided from an outside source, fuel cells never “run down.” They keep on producing electricity as long as fuel is fed to them.

Newer fuel cells, such as the cell in the **problem-solving LAB** and the cell shown in **Figure 21-12**, use a plastic sheet called a proton-exchange membrane,

**Figure 21-12**

**a** In this fuel cell, hydrogen is the fuel. The half-reactions are separated by a proton-exchange membrane so that the electrons lost in oxidation flow through an external circuit to reach the site of reduction. As electrons travel through the external circuit, they can do useful work, such as running electric motors. The byproduct of this redox reaction is water, a harmless substance. **b** A “stack” of PEM-type cells can generate enough energy to power an electric car.



## Interpreting Scientific Illustrations

### Can the simplest atom power a car?

Daimler–Chrysler’s NECAR IV may be a preview of the future of automobiles. The NECAR IV is a compact car that is powered by a hydrogen fuel cell (HFC). This model can reach speeds of 90 mph (145 km/h), carry up to five passengers and cargo, and travel 280 miles (450 km) before refueling. It runs on oxygen from the air and pure hydrogen supplied in a tank. Its exhaust is water, making it pollution free.

### Analysis

To power a 1200-kg automobile, a hydrogen fuel cell must produce about 144 volts. Although the

cell potential for a hydrogen fuel cell is 1.229 V, approximately 43% of that voltage is lost to the production of heat, meaning that each cell’s actual potential is closer to 0.7 V. To generate enough voltage to power a car, the HFCs must be stacked, similar to the stack shown in **Figure 21-12b**.

When the electrodes are connected to a device, such as an electric motor, the electrons, which cannot travel through the PEM, travel through the external circuit and turn the motor.

### Thinking Critically

1. How many cells would be needed to power a 1200-kg automobile? What would be the length of the stack if one cell is 1.2 mm thick? Is it small enough to fit under the hood?
2. Compare and contrast a stack of cells with a voltaic pile.

or PEM, instead of a liquid electrode to separate the reactions. PEMs are not corrosive and they are safer and lighter in weight than liquid electrodes. Hydrogen ions ( $H^+$ ) are protons, and they can pass directly through the membrane from the anode (where hydrogen is oxidized) to the cathode. There, they combine with oxygen molecules and electrons returning from the external circuit to form water molecules, which are released as steam.

One potential application for fuel cells is as an alternative power source for automobiles. However, as the **Chemistry and Technology** feature at the end of this chapter explains, scientists must resolve some fundamental challenges before fuel cells power the cars we drive.

## Corrosion

So far in this chapter, you have examined the spontaneous redox reactions in voltaic cells. Spontaneous redox reactions also occur in nature. A prime example is corrosion, usually called rusting, of iron. **Corrosion** is the loss of metal resulting from an oxidation–reduction reaction of the metal with substances in the environment. Although rusting is usually thought of as a reaction between iron and oxygen, it is more complex. Can you recall ever seeing or reading about corrosion happening in perfectly dry air or in water that contains no dissolved oxygen? Probably not because both water and oxygen must be present for rusting to take place. For this reason, the steel hulls of ships, such as that shown in **Figure 21-13**, are especially susceptible to corrosion in the form of rust.

Rusting usually begins where there is a pit or small break in the surface of the iron. This

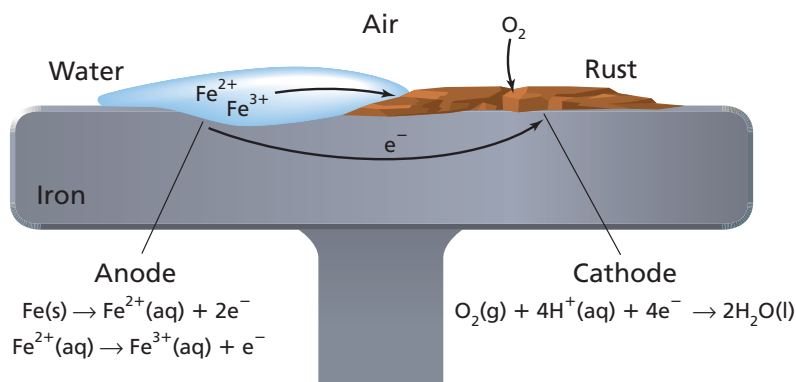
**Figure 21-13**

The steel hull of oceangoing ships offers strength, reliability, and durability, but steel is susceptible to corrosion. Ships such as this one in St. John Harbour, New Brunswick, Canada, often show the telltale sign of corrosion, which is rust.

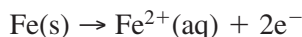


**Figure 21-14**

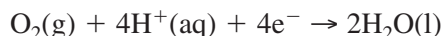
Corrosion occurs when air, water, and iron set up a voltaic cell similar to the conditions shown at the surface of this iron I-beam.



region becomes the anode of the cell as iron atoms begin to lose electrons, as illustrated in **Figure 21-14**.



The iron(II) ions become part of the water solution while the electrons move through the iron to the cathode region. In effect, the piece of iron becomes the external circuit as well as the anode. The cathode is usually located at the edge of the water drop where water, iron, and air come in contact. Here, the electrons reduce oxygen from the air in this half-reaction.

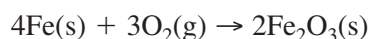


The supply of H<sup>+</sup> ions is probably furnished by carbonic acid formed when CO<sub>2</sub> from the air dissolves in water.

Next, the Fe<sup>2+</sup> ions in solution are oxidized to Fe<sup>3+</sup> ions by reaction with oxygen dissolved in the water. The Fe<sup>3+</sup> ions combine with oxygen to form insoluble Fe<sub>2</sub>O<sub>3</sub>, rust.



Combining the three equations yields the overall cell reaction for the corrosion of iron.



You can observe the process of corrosion first-hand by performing the **miniLAB** that results in the corrosion of an iron nail.

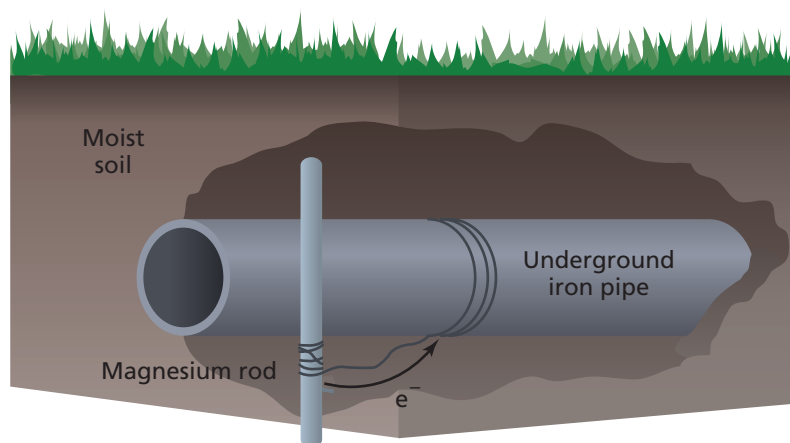


**a**

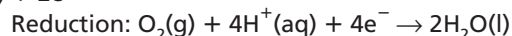
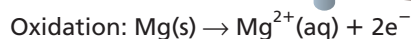
**Figure 21-15**

Because corrosion can cause considerable damage, it is important to investigate ways to prevent rust and deterioration.

- a** Paint or another protective coating is one way to protect steel structures from corrosion.
- b** Sacrificial anodes of magnesium or other active metals are also used to prevent corrosion.



**b**



Rusting is a rather slow process because water droplets have few ions and therefore are not good electrolytes. However, if the water contains abundant ions, as in seawater or in regions where roads are salted in winter, corrosion occurs much faster because the solutions are excellent electrolytes.

It has been estimated that corrosion of cars, bridges, ships, the structures of buildings, and other metallic objects costs more than 100 billion dollars a year in the U.S. alone. For this reason, people have devised several means to minimize corrosion. One is simply to apply a coat of paint to seal out both air and moisture, but, because paint deteriorates, objects such as the ship's hull shown in **Figure 21-15a** must be repainted often.

The steel hulls of ships are constantly in contact with saltwater, so the prevention of corrosion is vital. Although the hull may be painted, another method is used to minimize corrosion. Blocks of metals, such as magnesium, aluminum, or titanium, that oxidize more easily than iron are placed in contact with the steel hull. These blocks rather than the iron in the hull become the anode of the corrosion cell. As a result, these blocks, called sacrificial anodes, are corroded while the iron in the hull is spared. Of course, the sacrificial anodes must be replaced before they corrode away completely, leaving the ship's hull unprotected. A similar technique is used to protect iron pipes that are run underground. Magnesium bars are attached to the pipe by wires, and these bars corrode instead of the pipe, as shown in **Figure 21-15b**.

Another approach to preventing corrosion is to coat iron with another metal that is more resistant to corrosion. In the **galvanizing** process, iron is

## miniLAB

### Corrosion

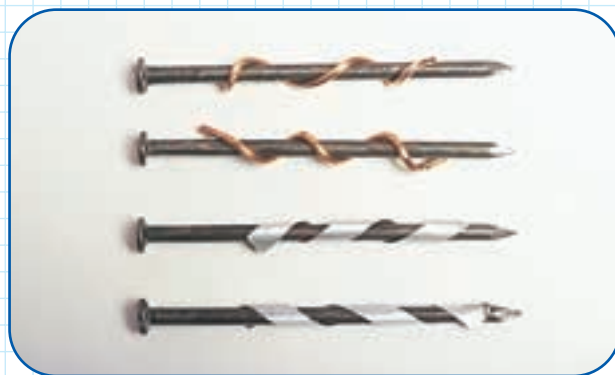
**Comparing and Contrasting** A lot of money is spent every year correcting and preventing the effects of corrosion. Corrosion is a real-world concern of which everyone needs to be aware.

**Materials** iron nails (4); magnesium ribbon (2 pieces, each about 5 cm long); copper metal (2 pieces, each about 5 cm long); 150-mL beakers (4); distilled water; saltwater solution; sandpaper.

#### Procedures



1. Use the sandpaper to buff the surfaces of each nail. Wrap two nails with the magnesium ribbon and two nails with the copper. Wrap the metals tightly enough so that the nails do not slip out.
2. Place each of the nails in a separate beaker. Add distilled water to one of the beakers containing a copper-wrapped nail and one of the beakers containing a magnesium-wrapped nail. Add enough distilled water to just cover the wrapped nails. Add saltwater to the other two beakers. Record your observations for each of the beakers.

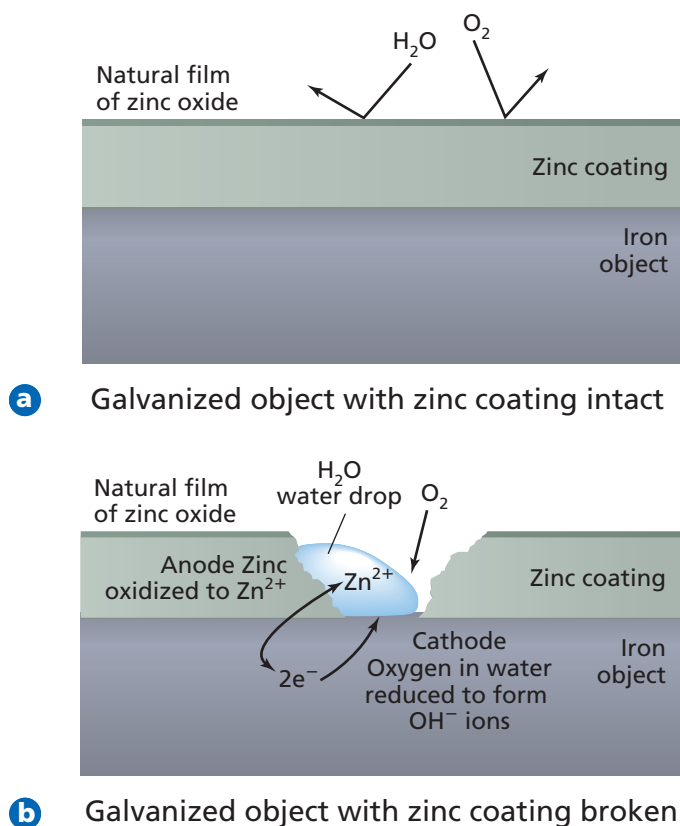


3. Let the beakers stand overnight in the warmest place available. Examine the nails and solutions the next day and record your observations.

#### Analysis

1. Describe the difference between copper-wrapped nails in the distilled water and saltwater after standing overnight.
2. Describe the difference between the magnesium-wrapped nails in the distilled water and saltwater.
3. In general, what is the difference between a copper-wrapped nail and a magnesium-wrapped nail?





**Figure 21-16**

Galvanizing helps prevent corrosion in two ways. **a** The zinc coating seals the iron from air and water by forming a barrier of zinc oxide that repels water and oxygen. **b** If the zinc coating breaks, the zinc acts as a sacrificial anode. **c** Metal objects that are left outside are often galvanized to prevent rust and corrosion caused by the elements.

coated with a layer of zinc by either dipping the iron object into molten zinc or by electroplating the zinc onto it. Although zinc is more readily oxidized than iron, it is one of the *self-protecting metals*, a group that also includes aluminum and chromium. When exposed to air, these metals oxidize at the surface, but the thin metal oxide coating clings tightly to the metal and seals it from further oxidation.

Galvanizing protects iron in two ways. As long as the zinc layer is intact, water and oxygen cannot reach the iron's surface. Inevitably, though, the zinc coating cracks. When this happens, zinc protects iron from rapid corrosion by becoming the anode of the voltaic cell set up when water and oxygen contact iron and zinc at the same time. **Figure 21-16** illustrates how these two forms of corrosion protection work.

## Section



## Assessment

- 14.** What is reduced and what is oxidized in the ordinary zinc–carbon dry cell battery? What features make the alkaline dry cell an improvement over the earlier type of dry cell battery?
- 15.** Explain how primary and secondary batteries differ. Give an example of each type.
- 16.** Explain why a fuel cell does not run down like other batteries.
- 17.** What is a sacrificial anode? How is one used?
- 18. Thinking Critically** Standard dry cell batteries have a relatively short shelf life. Explain why older dry-cell batteries may not have the same power output as newer batteries. How can the shelf life of these batteries be extended?
- 19. Calculating** Use data from **Table 21-1** to calculate the cell potential of the hydrogen–oxygen fuel cell described in this section.

In Section 21.2, you learned that rechargeable batteries can regain their electrical potential and be reused. You learned that a current can be introduced to cause the reverse reaction, which is not spontaneous, to happen. This aspect of electrochemistry—the use of an external force, usually in the form of electricity, to drive a chemical reaction—is important and has many practical applications.

## Reversing Redox Reactions

When a battery generates electricity, electrons given up at the anode flow through an external circuit to the cathode where they are used in a reduction reaction. A secondary battery is one that can be recharged by passing a current through it in the opposite direction. The current source can be a generator or even another battery. The energy of this current reverses the cell redox reaction and regenerates the battery's original substances.

To understand this process, look at **Figure 21-17**, which shows an electrochemical cell powering a light bulb by a spontaneous redox reaction. The beakers on the left contain a zinc strip in a solution of zinc ions. The beakers on the right contain a copper strip in a solution of copper ions. You saw in Section 21.1 how electrons in this system flow from the zinc side to the copper side, creating an electric current. As the reaction continues, the zinc strip deteriorates, while copper from the copper ion solution is deposited as copper metal on the copper strip. Over time, the flow of electrons decreases and the strength of the electrical output diminishes to the point that the bulb will not light. However, the cell can be regenerated if current is applied in the reverse direction using an external voltage source. The reverse reaction is nonspontaneous, which is why the voltage source is required. If the voltage source remains long enough, eventually the cell will return to near its original strength and can again produce electrical energy to light the bulb.

The use of electrical energy to bring about a chemical reaction is called **electrolysis**. An electrochemical cell in which electrolysis occurs is called an **electrolytic cell**. For example, when a secondary battery is recharged, it is acting as an electrolytic cell.

## Objectives

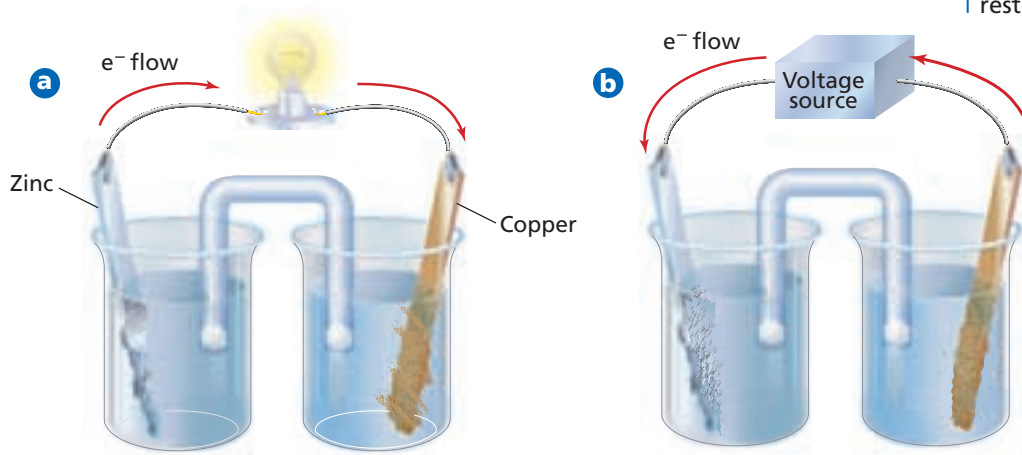
- **Describe** how it is possible to reverse a spontaneous redox reaction in an electrochemical cell.
- **Compare** the reactions involved in the electrolysis of molten sodium chloride with those in the electrolysis of brine.
- **Discuss** the importance of electrolysis in the smelting and purification of metals.

## Vocabulary

electrolysis  
electrolytic cell

**Figure 21-17**

**a** Electrons in this zinc–copper electrochemical cell flow from the zinc strip to the copper strip, causing an electric current that powers the light bulb. As the spontaneous reaction continues, much of the zinc strip is oxidized to zinc ions and the copper ions are reduced to copper metal, which is deposited on the copper strip. **b** If an outside voltage source is applied to reverse the flow of electrons, the original conditions of the cell are restored.



## History

### CONNECTION

**E**lectrolysis can be useful to clean historic objects recovered from shipwrecks. Coatings of salts from the seawater on metal objects are removed by an electrochemical process. A voltaic cell is set up with a cathode that is the object itself and a stainless steel anode in a basic solution. Chloride ions are removed when the electric current is turned on.

In another process, bacteria convert sulfate ions to hydrogen sulfide gas and cause silver coins and bars to become coated with silver sulfide after long periods of time at the bottom of the ocean. In an electrolytic cell, the silver in silver sulfide can be reduced to silver metal and reclaimed.



## Applications of Electrolysis

Recall that the voltaic cells convert chemical energy to electrical energy as a result of a spontaneous redox reaction. Electrolytic cells do just the opposite: they use electrical energy to drive a nonspontaneous reaction. A common example is the electrolysis of water. In this case, an electric current decomposes water into hydrogen and oxygen.



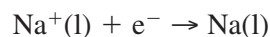
The electrolysis of water is one method by which hydrogen gas can be generated for commercial use. Aside from the decomposition of water, electrolysis has many other practical applications.

**Electrolysis of molten NaCl** Just as electrolysis can decompose water into its elements, it also can separate molten sodium chloride into sodium metal and chlorine gas. This process, the only practical way to obtain elemental sodium, is carried out in a chamber called a Down's cell, as shown in **Figure 21-18**. The electrolyte in the cell is the molten sodium chloride itself. Remember that ionic compounds can conduct electricity only when their ions are free to move, such as when they are dissolved in water or are in the molten state.

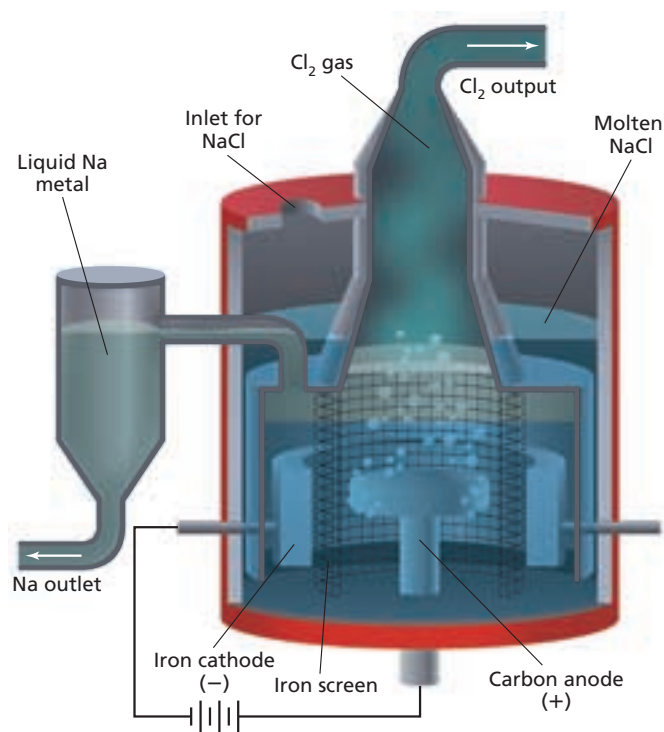
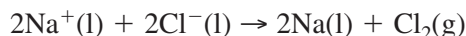
The anode reaction of the Down's cell is the oxidation of chloride ions.



At the cathode, sodium ions are reduced to atoms of sodium metal.

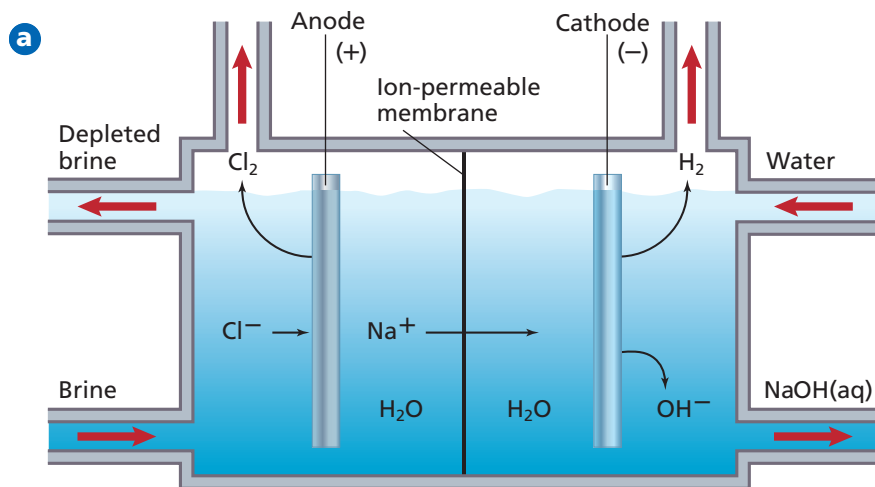


The net cell reaction is



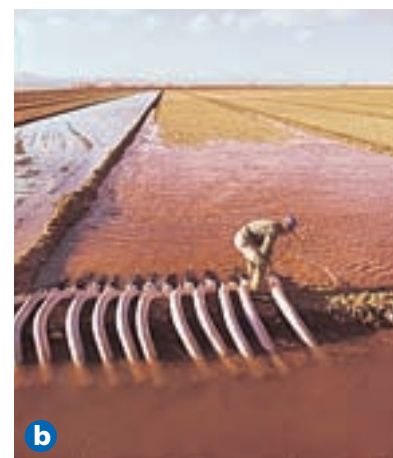
**Figure 21-18**

In a Down's cell, electrons supplied by a generator are used to reduce sodium ions. As electrons are removed from the anode, chloride ions are oxidized to chlorine gas.

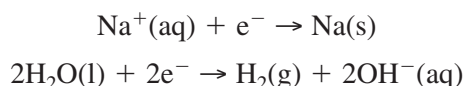


**Figure 21-19**

- a** Commercial facilities use an electrolytic process to derive hydrogen gas, chlorine gas, and sodium hydroxide from brine. **b** Chlorine gas is used to manufacture polyvinyl chloride products such as these irrigation pipes. **c** Sodium hydroxide is the key ingredient in drain cleaners.

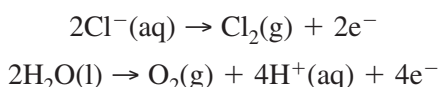


**Electrolysis of brine** The decomposition of brine, an aqueous solution of sodium chloride, is another process that is accomplished by electrolysis. **Figure 21-19** illustrates the electrolytic cell and products of the electrolysis of brine. Two reactions are possible at the cathode, the reduction of sodium ions and the reduction of hydrogen in water molecules.



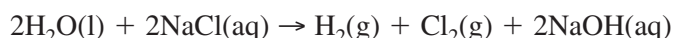
Here, a key product of reduction is hydrogen gas.

Two reactions are possible at the anode, the oxidation of chloride ions and the oxidation of oxygen in water molecules.



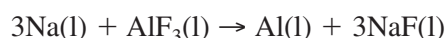
When the concentration of chloride ions is high, the primary product of oxidation is chlorine gas. However, as the brine solution becomes dilute, oxygen gas becomes the primary product.

To appreciate the commercial importance of this process, look at the overall cell reaction.



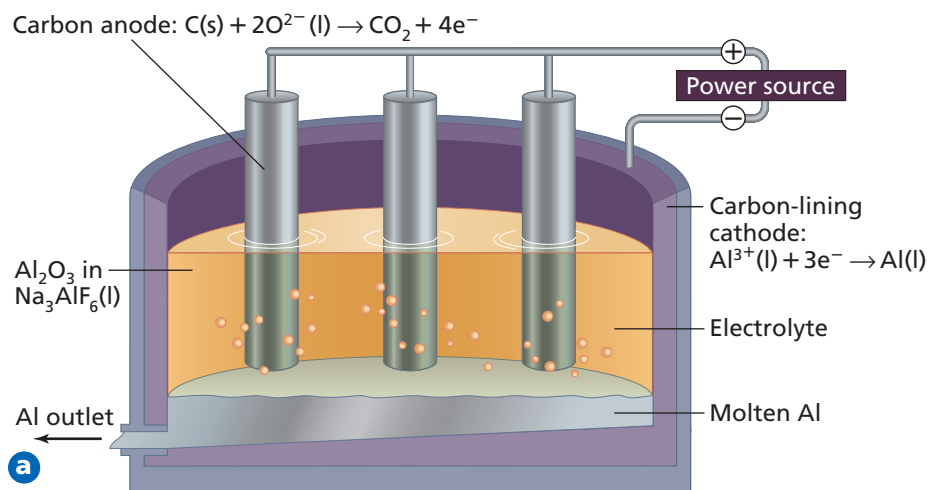
All three products of the electrolysis of brine—hydrogen gas, chlorine gas, and sodium hydroxide—are substances that are commercially important to industry.

**Aluminum manufacture** Aluminum is the most abundant metallic element in Earth's crust, but until the late nineteenth century, aluminum metal was more precious than gold. Aluminum was expensive because no one knew how to purify it in large quantities. Instead, it was produced by a tedious and expensive small-scale process in which metallic sodium was used to reduce aluminum ions in molten aluminum fluoride to metallic aluminum.



In 1886, 22-year-old Charles Martin Hall (1863–1914) developed a process to produce aluminum by electrolysis using heat from a blacksmith



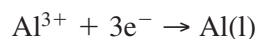


**Figure 21-20**

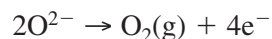
**a** Aluminum is produced by the Hall-Héroult process in cells similar to this one. Note that the cathode is the carbon (graphite) lining of the cell itself. **b** Every ton of aluminum that is recycled saves huge quantities of electrical energy that would be spent to produce new aluminum from ore.

forge, electricity from home-made batteries, and his mother's iron skillet as electrodes. At almost the same time, one of Le Châtelier's students, Paul L. T. Héroult (1863–1914), also 22 years old, discovered the same process. Today, it is called the Hall-Héroult process, which is illustrated in **Figure 21-20**.

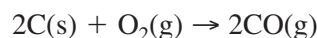
In the modern version of this process, aluminum metal is obtained by electrolysis of aluminum oxide, which is refined from bauxite ore ( $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ ). The aluminum oxide is dissolved at  $1000^\circ\text{C}$  in molten synthetic cryolite ( $\text{Na}_3\text{AlF}_6$ ), another aluminum compound. The cell is lined with graphite, which forms the cathode for the reaction. Another set of graphite rods is immersed in the molten solution as an anode. The following half-reaction occurs at the cathode.



The molten aluminum settles to the bottom of the cell and is drawn off periodically. Oxide ions are oxidized at the cathode in this half-reaction.

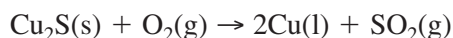


Because temperatures are high, the liberated oxygen reacts with the carbon of the anode to form carbon monoxide.



The Hall-Héroult process uses huge amounts of electric energy. For this reason, aluminum often is produced in plants built close to large hydroelectric power stations, where electric energy is abundant and less expensive. The vast amount of electricity needed to produce aluminum from ore is the prime reason that it is especially important to recycle aluminum. Recycled aluminum already has undergone electrolysis, so the only energy required to make it usable again is the heat used to melt it in a furnace.

**Purification of ores** Another application of electrolysis is in the purification of metals such as copper. Most copper is mined in the form of the ores chalcopyrite ( $\text{CuFeS}_2$ ), chalcocite ( $\text{Cu}_2\text{S}$ ), and malachite ( $\text{Cu}_2\text{CO}_3(\text{OH})_2$ ). The sulfides are most abundant and yield copper metal when heated strongly in the presence of oxygen.



The copper from this process contains many impurities and must be refined, so the molten copper is cast into large, thick plates. These plates are then used as an anode in an electrolytic cell containing a solution of copper(II) sulfate. The cathode of the cell is a thin sheet of pure copper. As current is passed through the cell, copper atoms in the impure anode are oxidized to copper(II) ions, which migrate through the solution to the cathode where they are reduced to copper atoms. These atoms become part of the cathode while impurities fall to the bottom of the cell.

**Electroplating** Objects can be electroplated with a metal such as silver in a method similar to that used to refine copper. The object to be silver plated is the cathode of an electrolytic cell that has a silver anode, as shown in **Figure 21-21**. At the cathode, silver ions present in the electrolyte solution are reduced to silver metal by electrons from an external power source. The silver forms a thin coating over the object being plated. The anode consists of a silver bar or sheet, which is oxidized to silver ions as electrons are removed by the power source. Current passing through the cell must be carefully controlled in order to get a smooth, even metal coating.



**Figure 21-21**

In an electrolytic cell used for silver plating, the object to be plated is the cathode where silver ions in the electrolyte solution are reduced to silver metal and deposited on the object.

## Section 21.3 Assessment

20. Define electrolysis and relate the definition to spontaneity of redox reactions.
21. What are the products of the electrolysis of brine? Of the electrolysis of molten sodium chloride? Explain why the reaction products differ.
22. Describe the process by which the copper that results from smelting of ore is purified by electrolysis.
23. **Thinking Critically** Suppose you want to plate an object with gold by electrolysis. What sort of substances would you need to have in the electrolyte solution? What would you use as the cathode and the anode of the cell?
24. **Inferring** Producing a kilogram of silver from its ions by electrolysis requires much less electrical energy than producing a kilogram of aluminum from its ions. Give a reason for this difference.

## Voltaic Cell Potentials

A voltaic cell converts chemical energy into electrical energy. It consists of two parts called half-cells. When two different metals, one in each half-cell, are used in the voltaic cell, a potential difference is produced. In this experiment, you will measure the potential difference of various combinations of metals used in voltaic cells and compare these values to the values found in the standard reduction potentials table.

### Problem

How can you measure the potential of voltaic cells?

### Objectives

- **Construct** voltaic cells using various combinations of metals for electrodes.
- **Design** the arrangement of the voltaic cells in a microplate in such a way as to use materials efficiently.
- **Determine** which metals are the anode and cathode in voltaic cells.
- **Compare** the experimental cell potential to the theoretical value found in Table 21-1.

### Materials

metal strips (approximately 0.6 cm by 1.3 cm) of copper, aluminum, zinc, and magnesium  
 1M copper(II) nitrate  
 1M aluminum nitrate  
 1M zinc nitrate  
 1M magnesium nitrate  
 24-well microplate  
 Beral-type pipette (5)

CBL System  
 voltage probe  
 filter paper (6 pieces size 0.6 cm by 2.5 cm)  
 1M potassium nitrate  
 forceps  
 steel wool or sandpaper  
 table of standard reduction potentials

### Safety Precautions



- Always wear goggles and an apron in the lab.
- The chemicals used in this experiment are eye and skin irritants. Wash thoroughly if they are spilled on the skin.

### Pre-Lab

1. Read the entire CHEMLAB.
2. Plan and organize how you will arrange voltaic cells in the 24-well microplate using the four metal combinations so that your time and materials will be used in the most efficient manner possible. Have your instructor approve your plan before you begin the experiment.
3. Prepare all written materials that you will take into the laboratory. Be sure to include safety precautions, procedure notes, and a data table similar to the example below in which to record your observations.
4. Review the definition of a voltaic cell.

Voltaic Cell Potential Data

Anode metal (black)	Cathode metal (red)	Actual cell potential (V)	Anode half-reaction and theoretical potential	Cathode half-reaction and theoretical potential	Theoretical cell potential	% Error

- Review the purpose of a salt bridge in the voltaic cell. In this experiment, the filter paper strips soaked in potassium nitrate are the salt bridges.
- Review the equation to calculate cell potential.
- For the voltaic cell  $\text{Mg}|\text{Mg}^{2+}||\text{Hg}^{2+}|\text{Hg}$ , identify which metal is the anode and which metal is the cathode. Which metal is being oxidized and which metal is being reduced? What is the theoretical potential for this voltaic cell?
- Review the equation to calculate percent error.

### Procedure

- Prepare the CBL to read potential differences (voltage). Plug the voltage probe into Channel 1. Turn the CBL on. Push the MODE button once to activate the voltmeter function.
- Soak the strips of filter paper in 2 mL of potassium nitrate solution. These are the salt bridges for the experiment. Use forceps to handle the salt bridges.
- Using the plan from your Pre-Lab, construct voltaic cells using the four metals and 1 mL of each of the solutions. Remember to minimize the use of solutions. Put the metals in the wells that contain the appropriate solution (for example, put the zinc metal in the solution with zinc nitrate). Use a different salt bridge for each voltaic cell. If you get a negative value for potential difference, switch the leads of the probe on the metals.
- Record which metals are the anode and cathode in each cell in the data table. The black lead of the probe will be attached to the metal that acts as the anode. The red lead will be attached to the cathode.
- Record the cell potential of each cell.

### Cleanup and Disposal

- Use forceps to remove the metals from the microplate.
- Rinse the solution off the metal pieces with water, then use steel wool or sandpaper to clean them.
- Rinse the wells of the microplate.
- Return each metal to its correct container.

### Analyze and Conclude

- Applying Concepts** Write the half-reactions for the anode and cathode in each of the voltaic cells in the data table. Look up the half-reaction potentials from the standard reduction potentials table (Table 21-1) and record these in the data table.
- Using Numbers** Calculate the theoretical potential for each voltaic cell and record it in the data table.
- Predicting** Using your data, rank the metals you used in order of most active to least active.
- Using Models** Calculate the percent error of the voltaic cell potential.
- Error Analysis** Why is the percent error calculated in step 4 large for some voltaic cells and small for others?

### Real-World Chemistry

- Why is lithium metal becoming a popular electrode in modern batteries? Use the standard reduction potentials table to help you answer this question.
- What type of battery is used in pacemakers to regulate a patient's heartbeat? What are some of the benefits of this battery?





# CHEMISTRY and Technology

## Fuel Cells

An important consideration for auto manufacturers today is fuel economy and pollution reduction. Fuel cells represent one option to achieve these goals.

Like a battery, a fuel cell produces electricity from a redox reaction. Unlike a battery, a fuel cell can generate electric current indefinitely because it oxidizes a continuous stream of fuel from an outside source.

### Fuel Cell Basics

Fuel cells can use several kinds of fuel, including natural gas and petroleum products. However, these are fossil fuels that produce carbon dioxide, an undesirable byproduct, when oxidized. Another drawback of common fuel cells is that they operate at temperatures from 200°C to 1000°C, and some contain hot, caustic, liquid electrolyte.

To avoid these problems, engineers have focused on a cell in which the fuel is hydrogen gas, the oxidant is oxygen from the air, and the product is water vapor. One of the more promising hydrogen fuel cells is one in which the half-cell reactions are separated by a thin polymer sheet called a proton-exchange membrane (PEM). The PEM fuel cell operates at approximately 100°C, and the moist membrane itself is the electrolyte.

On the anode side of the membrane, a platinum catalyst causes  $H_2$  molecules to dissociate into atoms. The PEM allows hydrogen protons to pass, while the electrons must travel an electrical circuit. On the cathode side of the membrane, the protons combine with oxygen from the air and the electrons from the circuit to form water.

### Making Fuel Cells Practical

Before PEM hydrogen fuel cells become practical, several issues must be resolved. PEM cells are expensive, in part because of the platinum powder that catalyzes the reaction. Safe storage and delivery of hydrogen is another key issue. The vehicle must carry enough hydrogen to power the vehicle over an acceptable range. Chemists are investigating ways to store and deliver hydrogen to fuel the cells. For example, carbon cage molecules in the form of balls or tubes can trap large quantities of hydrogen. When pressure is reduced



and the temperature is raised, these cages release the hydrogen in gaseous form.

Probably the most critical consideration is the hydrogen source. Unfortunately, much of the hydrogen gas produced commercially comes from the hydrocarbons of fossil fuels, which defeats the goal of fossil fuel conservation. Hydrogen can be produced from water by electrolysis, but this requires electrical energy that is produced by processes involving the combustion of fossil fuels. Clearly, a suitable method of hydrogen production is required. However, even with their present limitations, fuel cells are a viable energy alternative for the future.

### Investigating the Technology

- 1. Thinking Critically** If electrolysis is a safe and technologically sound method to generate hydrogen gas, how might the process be made more environmentally safe and economically practical?
- 2. Using Resources** Investigate the technology of carbon cage molecules, including fullerenes and nanotubes, and elaborate on their utility in hydrogen fuel cells.



**CLICK HERE**

Visit the Chemistry Web site at [science.glencoe.com](http://science.glencoe.com) to find links about hydrogen fuel cells.

## Summary

### 21.1 Voltaic Cells

- In a voltaic cell, the oxidation and reduction half-reactions of a redox reaction are separated and ions flow through a salt-bridge conductor.
- In a voltaic cell, oxidation takes place at the anode, and reduction takes place at the cathode.
- The standard potential of a half-cell reaction is the voltage it generates when paired with a standard hydrogen electrode. Standard potentials are measured at 25°C and 1 atm pressure with a 1M concentration of ions in the half-cells.
- The reduction potential of a half-cell is negative if it undergoes oxidation connected to a standard hydrogen electrode. The reduction potential of a half-cell is positive if it undergoes reduction when connected to a standard hydrogen electrode.
- The standard potential of a voltaic cell is the difference between the standard reduction potentials of the half-cell reactions.

### 21.2 Types of Batteries

- Batteries are voltaic cells packaged in a compact, usable form.
- A battery can consist of a single cell or multiple cells.
- Primary batteries can be used only once, whereas secondary batteries can be recharged.
- When a battery is recharged, electrical energy supplied to the battery reverses the direction of the redox reaction that takes place when the battery is delivering current. Thus, the original reactants are restored.

- Fuel cells are batteries in which the substance oxidized is a fuel such as hydrogen.
- Iron can be protected from corrosion: by applying a coating of another metal or paint to keep out air and water, or by attaching a piece of metal (a sacrificial anode) that is oxidized more readily than iron.

### 21.3 Electrolysis

- Electrical energy can be used to bring about non-spontaneous redox reactions that produce useful products. This process is called electrolysis and takes place in an electrolytic cell.
- Metallic sodium and chlorine gas may be obtained by the electrolysis of molten sodium chloride.
- Electrolysis of strong aqueous sodium chloride solution (brine) yields hydrogen gas and hydroxide ions at the cathode while producing chlorine gas at the anode.
- Metals such as copper can be purified by making them the anode of an electrolytic cell where they are oxidized to ions, which are then reduced to pure metal at the cathode.
- Objects can be electroplated by making them the cathode of an electrolytic cell in which ions of the desired plating metal are present.
- Aluminum is produced by the electrolysis of aluminum oxide. The process uses a great amount of electrical energy.

## Key Equations and Relationships

- Potential of a voltaic cell (p. 669)  $E_{\text{cell}}^0 = E_{\text{reduction}}^0 - E_{\text{oxidation}}^0$

## Vocabulary

- anode (p. 665)
- battery (p. 672)
- cathode (p. 665)
- corrosion (p. 679)
- dry cell (p. 673)
- electrochemical cell (p. 665)
- electrolysis (p. 683)
- electrolytic cell (p. 683)
- fuel cell (p. 677)
- galvanizing (p. 681)
- half-cell (p. 665)
- primary battery (p. 675)
- reduction potential (p. 666)
- salt bridge (p. 664)
- secondary battery (p. 675)
- standard hydrogen electrode (p. 666)
- voltaic cell (p. 665)

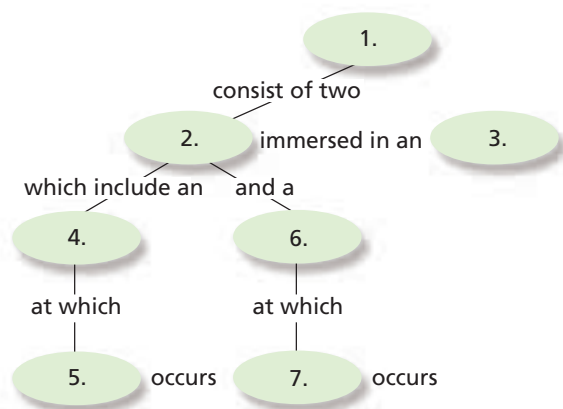


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## Concept Mapping

25. Complete the concept map using the following terms: reduction, electrodes, electrochemical cells, anode, oxidation, cathode, electrolyte.



## Mastering Concepts

26. What feature of an oxidation–reduction reaction allows it to be used to generate an electric current? (21.1)
27. Describe the process that releases electrons in a zinc–copper voltaic cell. (21.1)
28. What is the function of a salt bridge in a voltaic cell? (21.1)
29. What information do you need in order to determine the standard voltage of a voltaic cell? (21.1)
30. In a voltaic cell represented by  $\text{Al}|\text{Al}^{3+}||\text{Cu}^{2+}|\text{Cu}$ , what is oxidized and what is reduced as the cell delivers current? (21.1)
31. Under what conditions are standard reduction potentials measured? (21.1)
32. What part of a zinc–carbon dry cell is the anode? Describe the reaction that takes place there. (21.2)
33. How do primary and secondary batteries differ? (21.2)
34. What substance is reduced in a lead–acid storage battery? What substance is oxidized? What substance, other than water, is produced in each reaction? (21.2)
35. List two ways that a fuel cell differs from an ordinary battery. (21.2)
36. What is galvanizing? How does galvanizing protect iron from corrosion? (21.2)
37. How can the spontaneous redox reaction of a voltaic cell be reversed? (21.3)
38. Why is an outside source of energy needed for electrolysis? (21.3)
39. Where does oxidation take place in an electrolytic cell? (21.3)
40. What reaction takes place at the cathode when molten sodium chloride is electrolyzed? (21.3)
41. Explain why the electrolysis of brine is done on a large scale at many sites around the world. (21.3)
42. Explain how recycling aluminum conserves energy. (21.3)

## Mastering Problems

### Voltaic Cells (21.1)

Use data from **Table 21-1** in the following problems. Assume that all half-cells are under standard conditions.

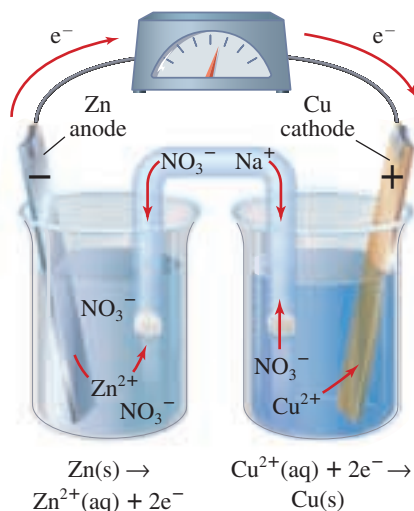
43. Write the standard cell notation for the following cells in which the half-cell listed is connected to the standard hydrogen electrode. An example is  $\text{Na}|\text{Na}^+||\text{H}^+|\text{H}_2$ .
  - a.  $\text{Zn}|\text{Zn}^{2+}$
  - b.  $\text{Hg}|\text{Hg}^{2+}$
  - c.  $\text{Cu}|\text{Cu}^{2+}$
  - d.  $\text{Al}|\text{Al}^{3+}$
44. Determine the voltage of the cell formed by pairing each of the following half-cells with the standard hydrogen electrode.
  - a.  $\text{Cr}|\text{Cr}^{2+}$
  - b.  $\text{Br}_2|\text{Br}^-$
  - c.  $\text{Ga}|\text{Ga}^{3+}$
  - d.  $\text{NO}_2|\text{NO}_3^-$
45. Determine whether each of the following redox reactions is spontaneous or nonspontaneous as written.
  - a.  $\text{Mn}^{2+} + 2\text{Br}^- \rightarrow \text{Br}_2 + \text{Mn}$
  - b.  $\text{Fe}^{2+} + \text{Sn}^{2+} \rightarrow \text{Fe}^{3+} + \text{Sn}$
  - c.  $\text{Ni}^{2+} + \text{Mg} \rightarrow \text{Mg}^{2+} + \text{Ni}$
  - d.  $\text{Pb}^{2+} + \text{Cu}^+ \rightarrow \text{Pb} + \text{Cu}^{2+}$

46. Calculate the cell potential of voltaic cells that contain the following pairs of half-cells.
- Chromium in a solution of  $\text{Cr}^{3+}$  ions; copper in a solution of  $\text{Cu}^{2+}$  ions
  - Zinc in a solution of  $\text{Zn}^{2+}$  ions; platinum in a solution of  $\text{Pt}^{2+}$  ions
  - A half-cell containing both  $\text{HgCl}_2$  and  $\text{Hg}_2\text{Cl}_2$ ; lead in a solution of  $\text{Pb}^{2+}$  ions
  - Tin in a solution of  $\text{Sn}^{2+}$  ions; iodine in a solution of  $\text{I}^-$  ions

## Mixed Review

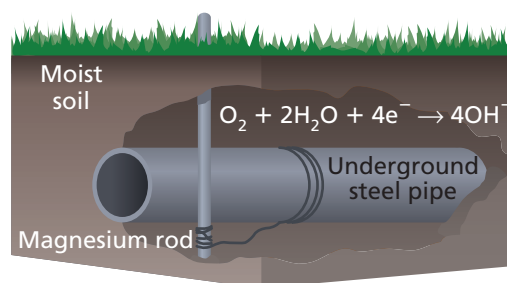
Sharpen your problem-solving skills by answering the following.

- Why do electrons flow from one electrode to the other in a voltaic cell?
- What substance is electrolyzed to produce aluminum metal?
- Write the oxidation and reduction half-reactions for a silver-chromium voltaic cell. Identify the anode, cathode, and electron flow.



- Primary cells are cells like the ordinary dry cell that cannot be recharged. Storage cells are cells like the nickel-cadmium cell or the lead-storage battery that can be recharged. Is the  $\text{Zn-Cu}^{2+}$  cell shown above a primary cell or a storage cell?
- Determine the voltage of the cell in which each of the following half-cells is connected to a  $\text{Ag}|\text{Ag}^+$  half-cell.
  - $\text{Be}^{2+}|\text{Be}$
  - $\text{S}|\text{S}^{2-}$
  - $\text{Au}^+|\text{Au}$
  - $\text{I}_2|\text{I}^-$

- Explain why water is necessary for the corrosion of iron.
- In the electrolytic refining of copper, what factor determines which piece of copper is the anode and which is the cathode?
- Explain how the oxidation of hydrogen in a fuel cell differs from the oxidation of hydrogen when it burns in air.
- Lead-acid batteries and other rechargeable batteries are sometimes called *storage batteries*. Precisely what is being stored in these batteries?
- Buried steel pipeline can be protected against corrosion by cathodic protection. In this process, the steel pipe is connected to a more active metal, such as magnesium, that would corrode instead of the steel. Use the diagram to answer the following questions.



- What is the cathode? What is the anode?
- Describe briefly how the magnesium metal protects the steel.

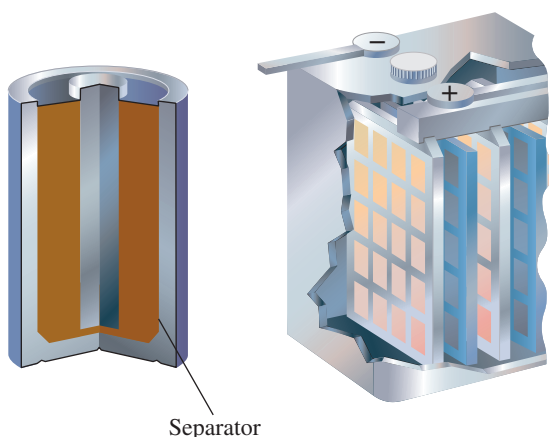
## Thinking Critically

- Communicating** Write two or three sentences describing the processes that take place in a voltaic cell and account for the direction of electron flow. Use the words *cathode*, *anode*, *oxidation*, *reduction*, and *potential difference* in your sentences.
- Predicting** How would standard reduction potentials be different if scientists had chosen the  $\text{Cu}^{2+}-\text{Cu}$  half-cell as a standard instead of the  $\text{H}^+-\text{H}_2$  half-cell? What would the potential of the hydrogen electrode be if the copper electrode were the standard? How would the relationships among the standard reduction potentials change?
- Applying Concepts** Suppose that you have a voltaic cell in which one half-cell is made up of a strip of tin immersed in a solution of tin(II) ions.
  - How could you tell by measuring voltage whether the tin strip was acting as a cathode or an anode in the cell?
  - How could you tell by simple observation whether the tin strip was acting as a cathode or an anode?



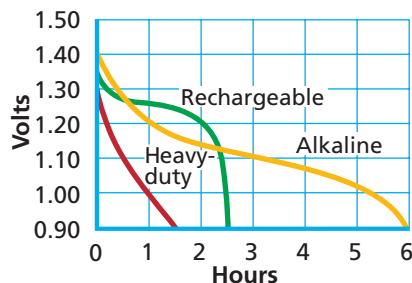
**60. Hypothesizing** The potential of a half-cell varies with concentration of reactants and products. For this reason, standard potentials are measured at 1M concentration. Maintaining a pressure of 1 atm is especially important in half-cells that involve gases as reactants or products. Suggest a reason that gas pressure is especially critical in these cells.

**61. Analyze and Conclude** Zinc–carbon, alkaline, mercury, lithium, and NiCad batteries all contain a separator between the anode and cathode that allows exchange of ions but keeps the anode and cathode reactants from mixing. No such separator is present (or needed) in a lead–acid battery.



Study the structures of this battery carefully and suggest a reason why no separator is required.

**62. Interpreting Graphs** Various commercial batteries were tested to determine how each would perform when operating a motorized toy. Use the graph below to determine which battery would be the best choice to operate the toy for a long period of time. Which battery goes dead abruptly?



**63. Hypothesizing** The density of a sample of electrolyte from a lead–acid battery is measured and found to be 1.09 g/mL. Do you think this density indicates a fully charged battery, partially discharged battery, or a “dead” battery? Give a reason for your choice.

**64. Drawing a Conclusion** The black tarnish that appears on silver is silver sulfide ( $\text{Ag}_2\text{S}$ ). A way to get rid of silver tarnish is to place the silver object into a pan lined with wrinkled aluminum foil and water in which some salt or baking soda has been dissolved. As the silver sits in contact with the aluminum foil, the black tarnish disappears where the object is immersed in the solution. Using what you have learned about electrochemistry, propose an explanation for this observation.

**65. Thinking Critically** Lead–acid storage batteries produce current with a voltage of about 12 volts. If you have a voltmeter in your car, you see that the meter reads about 14 V while the car is running normally. Suggest an explanation for this higher voltage reading.

**66. Applying Concepts** During electrolysis, an electrolytic cell gives off bromine vapor and hydrogen gas. After electrolysis, the cell is found to contain a concentrated solution of potassium hydroxide. What was the composition of the cell before electrolysis began?

**67. Hypothesizing** Instead of galvanizing iron, it can be plated with copper to protect it. What would happen when the copper coating became broken or cracked? Would the copper continue to protect the iron as zinc does? Explain fully.

## Writing in Chemistry

**68.** Research the commercial process of electroplating silver in the costume jewelry industry. Write a summary of your findings, including a diagram.

**69.** Several years ago, the supporting structure of the Statue of Liberty became so corroded that it had to be replaced entirely. Find out what the structure was and why it corroded so badly. Write a report that discusses the chemical processes involved and include a timeline of the statue, starting before 1886 in France.

## Cumulative Review

*Refresh your understanding of previous chapters by answering the following.*

**70.** If the volume of a sample of chlorine gas is 8.2 L at 1.2 atm and 306 K, what volume will the gas occupy at STP? (Chapter 14)

**71.** According to the collision model of chemical reactions, how is it possible that two molecules may collide but not react? (Chapter 17)

Use these questions and the test-taking tip to prepare for your standardized test.

1. A salt bridge is essential to a voltaic cell for all of the following reasons EXCEPT \_\_\_\_\_.
  - a. it allows ions to move from the solution of one cell to the other
  - b. it causes electric current to flow between the two electrodes of a cell
  - c. it relieves the buildup of positive charge on the anode side of the cell
  - d. it allows electrons to move from the solution of one cell to the other

**Using Tables** Use the table to answer questions 2–5.

Selected Standard Reduction Potentials at 25°C, 1 atm, and 1M Ion Concentration	
Half-Reaction	$E^0$ (V)
$\text{Mg}^{2+} + 2e^- \rightarrow \text{Mg}$	-2.372
$\text{Al}^{3+} + 3e^- \rightarrow \text{Al}$	-1.662
$\text{Pb}^{2+} + 2e^- \rightarrow \text{Pb}$	-0.1262
$\text{Ag}^+ + e^- \rightarrow \text{Ag}$	0.7996
$\text{Hg}^{2+} + 2e^- \rightarrow \text{Hg}$	0.851

2. Which of the metal ions is most easily reduced?
  - a.  $\text{Mg}^{2+}$
  - b.  $\text{Hg}^{2+}$
  - c.  $\text{Ag}^+$
  - d.  $\text{Al}^{3+}$
3. On the basis of the standard reduction potentials shown above, which of the following standard cell notations below correctly represents its voltaic cell?
  - a.  $\text{Ag} \mid \text{Ag}^+ \parallel \text{Al}^{3+} \mid \text{Al}$
  - b.  $\text{Mg} \mid \text{Mg}^{2+} \parallel \text{H}^+ \mid \text{H}_2$
  - c.  $\text{H}_2 \mid \text{H}^+ \parallel \text{Pb}^{2+} \mid \text{Pb}$
  - d.  $\text{Pb} \mid \text{Pb}^{2+} \parallel \text{Al}^{3+} \mid \text{Al}$
4. A voltaic cell consists of a magnesium bar dipping into a 1M  $\text{Mg}^{2+}$  solution and a silver bar dipping into a 1M  $\text{Ag}^+$  solution. What is the standard potential of this cell?
  - a. 1.572 V
  - b. 3.172 V
  - c. 0.773 V
  - d. 3.971 V

5. Assuming standard conditions, which of the following cells will produce a potential of 2.513 V?
  - a.  $\text{Al} \mid \text{Al}^{3+} \parallel \text{Hg}^{2+} \mid \text{Hg}$
  - b.  $\text{H}_2 \mid \text{H}^+ \parallel \text{Hg}^{2+} \mid \text{Hg}$
  - c.  $\text{Mg} \mid \text{Mg}^{2+} \parallel \text{Al}^{3+} \mid \text{Al}$
  - d.  $\text{Pb} \mid \text{Pb}^{2+} \parallel \text{Ag}^+ \mid \text{Ag}$
6. Which of the following statements is NOT true of batteries?
  - a. Batteries are compact forms of voltaic cells.
  - b. Secondary batteries also are known as storage batteries.
  - c. Batteries can consist only of a single cell.
  - d. The redox reaction in a rechargeable battery is reversible.
7. The corrosion, or rusting, of iron is an example of a naturally occurring voltaic cell. To prevent corrosion, sacrificial anodes are sometimes attached to rust-susceptible iron. Sacrificial anodes must \_\_\_\_\_.
  - a. be more likely to be reduced than iron
  - b. have a higher reduction potential than iron
  - c. be more porous and abraded than iron
  - d. lose electrons more easily than iron
8. A strip of metal X is immersed in a 1M solution of  $\text{X}^+$  ions. When this half-cell is connected to a standard hydrogen electrode, a voltmeter reads a positive reduction potential. Which of the following is true of the X electrode?
  - a. It accepts electrons more readily than  $\text{H}^+$  ions.
  - b. It is undergoing oxidation.
  - c. It is adding positive  $\text{X}^+$  ions to its solution.
  - d. It acts as the anode in the cell.
9. To electroplate an iron fork with silver, which of the following is true?
  - a. The silver electrode must have more mass than the fork.
  - b. The iron fork must act as the anode in the cell.
  - c. Electrical current must be applied to the iron fork.
  - d. Iron ions must be present in the cell solution.



### TEST-TAKING TIP

**Your Mistakes Can Teach You** The mistakes you make before the test are helpful because they show you the areas in which you need more work. When calculating the standard potential of an electrochemical cell, remember that coefficients do not change the standard reduction potentials of the half-reactions.